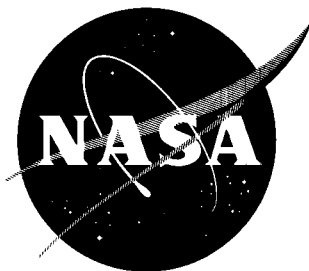


N63-17340

NASA TN D-1785



TECHNICAL NOTE

D-1785

INVESTIGATION OF MECHANICAL PROPERTIES
AND METALLURGICAL CHARACTERISTICS OF A METALLIC CHROMIUM
AND MAGNESIUM OXIDE COMPOSITE

By Charles R. Manning, Jr., and Dick M. Royster

Langley Research Center
Langley Station, Hampton, Va.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON

June 1963

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNICAL NOTE D-1785

INVESTIGATION OF MECHANICAL PROPERTIES
AND METALLURGICAL CHARACTERISTICS OF A METALLIC CHROMIUM
AND MAGNESIUM OXIDE COMPOSITE

By Charles R. Manning, Jr., and Dick M. Royster

SUMMARY

An experimental investigation has been made to evaluate an uncoated thin composite sheet material containing metallic chromium and magnesium oxide for aerospace applications in the temperature range where coated refractory metals also are being considered. The evaluation consisted of mechanical property tests both at room and elevated temperatures up to 2600° F. The effect of preoxidation at various temperatures on the room-temperature properties is shown. Bend and tensile transition temperatures were also determined and static oxidation tests were performed up to 2800° F. The metallurgical study included identification of the oxide films by X-ray analysis and also a study of the solid-state reactions taking place between the chromium and the ceramic material by the use of light and electron microscopy. Fabrication of the composite is discussed briefly. A description of the equipment and procedures utilized in performing the evaluation tests is included.

INTRODUCTION

In the aerospace industry there exists a great need for structural sheet materials that can be used at temperatures up to 3000° F and exhibit excellent resistance to oxidation. Current refractory metal sheet alloys, such as those of columbium and molybdenum, have good load-carrying capability in this temperature range, but these alloys require oxidation-resistant protective coatings which restrict their usefulness.

A new uncoated metal-ceramic composite sheet material has been developed for structural applications to 3000° F. This material is composed of a chromium matrix surrounding dispersed magnesium oxide particles and is reported (ref. 1) to have a relatively high melting temperature (3700° F), a low density (0.241 lb/in.³), and superior resistance to oxidation.

An investigation was undertaken at the NASA Langley Research Center to explore the capabilities and limitations of this new composite sheet material. The investigation included the determination of tensile properties up to 2600° F,

the determination of transition temperatures, and the determination of oxidation properties as well as X-ray diffraction and microstructure studies. A few checks on the fabrication characteristics were also included. The results of this investigation are presented herein.

MATERIAL AND SPECIMENS

The material utilized in this investigation was obtained from the manufacturer in two forms, 0.020-inch-thick sheet and 5/8-inch-diameter bar stock. The material is referred to herein as a chromium and magnesium oxide composite (Cr-MgO). The original sheet and bar material has a nominal composition of 95-percent chromium and 5-percent magnesium oxide by weight. A small amount of a similar material in bar form was tested; its composition differed from the sheet material in that 2/3 of 1 percent yttrium was added in an effort to improve its resistance to oxidation. The processing of the material used in this investigation is described in a subsequent section.

The three types of tensile specimens used in this investigation are shown in figure 1. The room-temperature sheet tensile specimen is shown in figure 1(a) and the elevated-temperature sheet tensile specimen is shown in figure 1(b). The elevated-temperature sheet tensile specimens were longer than the room-temperature specimens for two reasons: (1) the length of the reduced section was longer to obtain a uniform temperature over a 1/2-inch gage length, and (2) the ends of the specimen were longer to permit attachment of the power leads. The bar tensile specimen is shown in figure 1(c). The bend-test specimens for determining transition temperature were 2 inches long, 1/2 inch wide, and 0.020 inch thick.

Three types of oxidation specimens were used in this investigation. For the static oxidation tests, 0.66-inch-square specimens were cut from the 0.020-inch-thick sheet and 1/8-inch-thick disk-shaped specimens were cut from the 5/8-inch-diameter bar stock. The dynamic-oxidation specimens were $1\frac{1}{4}$ -inch-diameter concave disks of 0.020-inch-thick sheet shaped as shown in figure 2.

The specimens used to study the fabrication characteristics of the Cr-MgO material were threaded fasteners, 1/4-inch-diameter bolts with nuts, machined from the 5/8-inch-diameter bar stock.

PROCESSING OF THE MATERIAL

The Cr-MgO composite used in this investigation has a composition of 95-percent chromium and 5-percent magnesium oxide by weight. The Cr-MgO composite was prepared by mechanically mixing electrolytic chromium powder and magnesium oxide powder. The powder mixture was then compacted and sintered into a billet. The billet was then extruded either into a 5/8-inch-diameter rod or into a $1\frac{3}{4}$ -inch by 1/2-inch rectangular bar for the production of the

sheet material. The bar was then hot rolled at 2000° F perpendicular to the extrusion direction to a thickness of 80 mils. This thickness was the lower limit of the rolling facility. The 80-mil sheet was then machined in a milling machine to almost 20 mils and was annealed at 1800° F for 1 hour. The final step in the sheet preparation was to sand the material to the specified 0.020-inch thickness. The amount of sheet material received for this investigation was 14 sheets which were 4 inches long, 2 inches wide, and 0.020 inch thick.

TEST PROCEDURE

Mechanical Property Tests

Tensile tests.- Tensile tests were conducted in a 10,000-pound-capacity screw-powered testing machine at a head speed corresponding to a strain rate of 0.005 per minute to the yield stress and at an increased head speed corresponding to a strain rate of 0.05 per minute to failure. Load was recorded autographically against strain for the room-temperature sheet tensile specimens and against extension for the elevated-temperature sheet specimens and for the bar specimens tested at low temperatures. Strain was measured by foil-backed SR-4 type strain gages cemented to the specimen. Extension was measured by the relative movement of the testing machine heads. Elevated-temperature sheet tensile specimens were resistance heated and held at test temperature approximately 1 minute before testing. All specimen temperatures were measured by an optical pyrometer; no emittance corrections were made.

Bend tests.- Bend tests were made in the 10,000-pound-capacity screw-powered testing machine by using the equipment shown in figure 3. The bend-test specimens were simply supported on 1/8-inch-diameter pins and were centrally loaded by a ram having a contact radius of 1/8 inch. Bending loads were applied at a head speed of 0.01 inch per minute. In the elevated-temperature bend test the specimens were heated by two banks of tungsten filament lamps, one bank on each side. For bend tests below room temperature, the specimen and fixture were placed in a bath of cold water or ice water. Thermocouples spot-welded to the specimen were used to measure temperatures above room temperature. In the low-temperature tests the specimen temperature was monitored by a thermometer placed in the water bath.

Oxidation Tests

Two types of oxidation tests were made and are defined as follows: Static-oxidation tests are defined as those tests made in static air in a vertical tube furnace with the lower end of the furnace tube closed. Dynamic-oxidation tests are defined as those tests made in an arc jet with air at high temperatures moving over the specimen at a high velocity.

Static tests.- The static-oxidation testing equipment is shown in figure 4. The specimens were suspended on a platinum wire in the furnace and the weight change was autographically recorded by a sensitive balancing system. In addition, all specimens were weighed before and after testing. Test time varied from 1 hour

to 24 hours over the temperature range of 2000° F to 2800° F. The oxidation specimens were sectioned after testing and the final thickness was measured by a micrometer on the light microscope to determine the amount of material lost to oxide formation. This oxide subsequently spalled on cooling. The threaded fasteners were tested similarly in the furnace for 1 hour at temperatures from 2000° F to 2600° F.

Dynamic tests.- Two dynamic-oxidation tests were made in the Langley 2,500-kilowatt arc jet. This facility, using a 6-inch-diameter water-cooled nozzle and water-cooled copper electrodes, produces a virtually uncontaminated air-stream having a velocity of 400 feet per second and temperatures up to 7000° F. The facility is described in detail in reference 2. For these tests the specimen and graphite sting shown in figure 2 were mounted on a water-cooled support. One specimen, located approximately 6 inches above the nozzle, was exposed for 5 minutes. The second specimen was raised relative to the nozzle to lower the test temperature and was exposed for 2 minutes. The operating power for both tests was 1,395 kilowatts. Specimen temperatures to 3000° F were measured by a platinum-platinum-rhodium thermocouple spot-welded to the back surface of the specimen. These measurements were checked by an optical pyrometer viewing the specimen surface during exposure. The pyrometer was also used to measure the temperatures above 3000° F.

Metallurgical Studies

Metallurgical studies were made as an aid in evaluating the mechanical properties and oxidation tests. These studies included X-ray diffraction studies, microstructure examination, and hardness measurements.

X-ray diffraction study.- Sections were removed from the tested oxidation specimens and from the as-received material. The flat faces of these sections were examined by X-ray diffraction in the following manner. The sections were placed in the GE XRD-5 diffractometer and were scanned by using a collimated copper $K\alpha$ X-ray beam with a nickel filter. A scanning angle of 15° to 165° was used and the diffraction pattern was recorded on a strip chart recorder. The patterns were indexed and the materials were identified by using the American Society of Testing Materials (ASTM) card data file.

Microstructure examination.- Additional sections were removed from the tested oxidation specimens and from the as-received material. The cut edges of these sections were ground to remove any cold work left by the cut-off operation. The sections were then mounted and mechanically polished. Each polished section was etched by heating it in warm water for 2 minutes and then immersing it in a solution of 66-percent glycerine and 34-percent hydrochloric acid for 20 to 60 seconds. Photomicrographs were taken at various magnifications from 75 to 1,000 diameters to show the detailed structure in the sectioned specimens.

Hardness measurements.- Hardness measurements were made on the previously mentioned polished sections with a microhardness tester. All hardness values are given in Knoop hardness.

Fabrication

The fabrication of the Cr-MgO composite was studied to determine the ease or difficulty that would be encountered in machining, welding, and forming this material into structural configurations useful in aircraft and spacecraft. Threaded fasteners were machined from the bar stock by using cutting speeds comparable to those normally used in machining cast iron. Thin sheets were joined by electron-beam welding with the following parameters:

Accelerating potential, kv	85
Beam current, milliamp	1.25
Welding rate, in./min	30
Beam deflection (along the weld), in.	0.025
Vacuum, mm Hg	10^{-4}

RESULTS AND DISCUSSION

Mechanical Properties

Tensile tests.- The results of the tensile tests of the Cr-MgO composite are presented in tables I to III and are shown in figures 5 to 8. The room-temperature stress-strain curves (fig. 5) show that sheet material preoxidized at 2000° F for 1 hour has strength at room temperature comparable to that of the as-received material, but preoxidizing the material at higher temperatures causes a loss in room-temperature strength. The results of the elevated-temperature tensile tests are shown as stress-extension curves in figure 6. A comparison of these curves with the room-temperature stress-strain curves of figure 5 indicates a very large loss of strength at 2000° F and above; the tensile yield strength at 2600° F drops to 1,600 psi. Figure 7 shows the results of the low-temperature tensile tests on the bar material. The results indicate that the yield strength of the bar and the sheet are comparable, but that the ultimate strength of the bar is approximately 20 percent higher. The curves in figures 5 to 7 show an abrupt change in the shape of the stress-strain and stress-extension curves beyond the yield stress. This change occurs when the strain rate is increased from 0.005 per minute to 0.05 per minute and indicates that the material is very sensitive to strain rate. Elongation measurements made on the sheet material (fig. 8) show that preoxidizing of the material at 2000° F and above decreases the room-temperature ductility. After preoxidation at 2400° F the room-temperature elongation drops to less than 0.5 percent. This condition indicates that an embrittling effect is taking place during elevated-temperature exposure.

The strength of the Cr-MgO composite is compared with that of a coated refractory alloy in figure 9. The alloy used for comparison is a molybdenum alloy containing 0.5-percent titanium (Mo-0.5 Ti); this alloy and tests thereof are described in reference 3. These materials are compared on a strength-weight basis from room temperature to 2600° F. The coated refractory metal alloy has a higher strength-weight ratio over the entire range. In fact, the strength-weight ratio for the coated refractory metal alloy at 2700° F is comparable to that of the Cr-MgO composite at 2100° F. These results indicate that the Cr-MgO composite

would not be preferred as a structural material either at low or high temperatures on a strength-weight basis.

Transition temperature.- Transition temperatures obtained from the bend and tensile tests are shown in figure 10. In order to determine the bend-transition temperature, the following criterion was used. A specimen that withstood a 60° bend, as shown in figure 10, without failure was considered to be at a temperature above the transition temperature, and one that failed before bending 60° was considered to be below the transition temperature. Similarly, tension specimens showing 4 percent or less elongation were considered to be below the tension transition temperature, and those having 4-percent elongation or greater were considered to be above the transition temperature. By referring to figure 10, it will be noted that three bend specimens, tested between 80° F and 84° F, failed before a bend angle of 21° was attained. Two other specimens tested at 86° F and 90° F withstood the maximum bend angle 71° that the fixture would allow. This result placed the transition temperature in bending at 85° F.

The elongation data of the three tensile tests made on bar material are also shown in figure 10. One specimen tested at 32° F had an elongation of 3.1 percent. Another specimen tested at 85° F showed 4.5-percent elongation, and hence, based on the criterion stated above, would be considered above the transition temperature. The third specimen was tested at 112° F and showed an elongation of 9.2 percent. Because of the limited amount of data and because the line joining the 85° F and 112° F points is very steep, it may be concluded that the tensile transition temperature lies between 75° F and 100° F.

Oxidation and Nitrogen Diffusion

Static tests.- The results of oxidation tests on the Cr-MgO composite are shown in figures 11 to 14. Figure 11 shows curves of weight gained plotted against time at temperatures ranging from 2000° F to 2800° F as well as curves for the same material tested by the manufacturer. The results obtained by the manufacturer at 2000° F (dashed curve, fig. 11) show a considerably lower oxidation rate than the results obtained in this investigation. Some of this difference may be attributed to the fact that the manufacturer's tests were performed in very dry air (dewpoint, 60° F) whereas the present tests were made in normal sea-level atmospheric air.

The results of the oxidation tests on the Cr-MgO plus yttrium material, shown in figure 12, indicate that the addition of yttrium does not improve the oxidation resistance. In fact, the yttrium appears to increase the rate of oxidation. At 2800° F the material containing yttrium gained 75 mg/cm^2 in 4 hours whereas the Cr-MgO gained only 48 mg/cm^2 in 24 hours.

The results of thickness measurements made on the Cr-MgO sheet material after static oxidation tests and after the removal of the oxide layer are presented in figure 13. The loss of material thickness is plotted against exposure time for temperatures ranging from 2000° F to 2800° F. As shown by the dashed curves, the material loss at 2000° F in a 24-hour period is very small. However, the loss of material increases rapidly at 2500° F and above. At 2800° F, 0.010 inch or 50 percent of the original sheet material is lost in less than 3 hours.

In addition to the oxide formation, metallurgical studies, described in a later section, revealed the formation of a diffusion layer between the oxide and the base material. This layer was identified as a supersaturated solid solution of nitrogen plus a precipitate of chromium nitride (Cr_2N). The nitrogen penetration data are also plotted in figure 13. Penetration of the nitrogen also increases rapidly with temperature and as shown by the solid curves, it increases at a rate much faster than that of the loss of the original material due to oxidation.

In figure 14, combinations of temperature and time which will cause a loss of 0.002 inch of material, or 10 percent of the original thickness due to oxidation are shown. Also shown is a curve of temperature-time combinations required for 0.010-inch penetration of the nitrogen or 50-percent penetration of the original material. The two curves are nearly coincident, and it can be concluded that the rate of nitrogen penetration is approximately 5 times that of the loss of original material due to oxidation. This penetration of nitrogen into the base material is believed to be the cause of the embrittlement noted in the room-temperature tensile tests after preoxidation at and above 2000° F.

Dynamic tests.— Two dynamic oxidation tests were made on the sheet material to determine whether use of the Cr-MgO material would be suitable in a leading-edge application. The tests were made in an airflow of 400 feet per second and the specimen temperatures reached 2800° F and 3200° F. The specimen which attained 2800° F in the 2-minute test remained relatively undamaged, whereas the specimen which attained 3200° F in the 5-minute test failed by melting and erosion. A view of the specimen before and after testing at 3200° F is shown in figure 15. It is concluded from these two tests that this material would not be satisfactory for long-time exposures over 3000° F.

Metallurgical Investigation

X-ray diffraction study.— The oxide film formed on the surface of the Cr-MgO composite during exposure to temperatures of 2000° F and above was identified by the X-ray diffraction study as a mixture of two oxides: chromite, Cr_2O_3 , and perchromite, MgCr_2O_4 . This film was also found to flake off on cooling from these temperatures. The difference in thermal expansion between the base material Cr-MgO and the material MgCr_2O_4 was considered to be the cause of the spalling of the surface oxide during cooling.

X-ray diffraction techniques were used to study the composition of the material in the following conditions: (1) as-received sheet, (2) sheet material with oxide film, (3) sheet surface after removal of the oxide film, and (4) sheet surface after removal of the oxide film and removal of 0.002 to 0.005 inch of the remaining material. The results of the X-ray diffraction measurements are presented in tables IV to VII. The values of the d-spacings calculated from the diffraction record for the as-received Cr-MgO material agree with the d-spacings on the ASTM X-ray cards for Cr and MgO. This agreement indicates that only chromium and magnesium oxide are present. Table V gives the d-spacing for the oxide film which by comparison with the ASTM cards is identified as a combination of

chromite Cr_2O_3 and the perchromite MgCr_2O_4 . The chromite Cr_2O_3 is a high-temperature stable oxide of chromium and is very adherent to chromium metal surfaces. The perchormite MgCr_2O_4 is a complex oxide formed at high temperatures by the combination of Cr_2O_3 and MgO and it has a normal spinel structure.

Table VI gives the X-ray diffraction data for the Cr-MgO material after removal of the oxide film. The same oxides were identified on the material surface as were found in the oxide film itself. In addition, three other diffraction lines which indicate the presence of Cr_2N were found. Table VII gives the X-ray diffraction data for the Cr-MgO material that had been oxidized 4 hours at 2500°F . The oxide film as well as 0.002 to 0.005 inch of the remaining material were removed. Comparisons of the measured d-spacings with those on the ASTM cards indicate the presence of MgCr_2O_4 as well as Cr_2N . There was no indication of Cr_2O_3 , but there was evidence of pure chromium. This condition indicates that the nitrogen and the oxygen have diffused into the basic material.

Microstructure.- A study of the microstructure of the Cr-MgO composite in various conditions was undertaken to determine the location of the oxides and nitride found by X-ray diffraction analysis and to study possible causes of embrittlement of the material after exposure to elevated temperatures. Figures 16 and 17 show the microstructure of the Cr-MgO composite sheet and the Cr-MgO plus yttrium composite bar stock, respectively, in the as-received condition. In these figures the magnesium oxide inclusions, which are dark, are very uniform in size (3 to 5 microns), and are dispersed uniformly throughout the structure. Figure 18 shows the microstructure of a specimen oxidized at 2000°F for 4 hours. At this temperature there is no indication of oxidation and no indication of nitride formation at the surface. This condition indicates that at 2000°F the solid-state diffusion of nitrogen and oxygen in this material is relatively low.

Figures 19 and 20 show two specimens that were oxidized for 1 hour and 4 hours, respectively, at 2500°F . Just below the surface a dark layer is shown; this area indicates that diffusion has taken place. The diffused layer is 0.0021 inch thick in the specimen exposed for 1 hour (fig. 19) and is 0.0054 inch thick in the specimen exposed for 4 hours (fig. 20). In the diffused areas there are straight lamellar precipitates running parallel within each grain, but the precipitates are oriented differently from grain to grain. The grain boundaries in this area appear to consist of the same precipitate as that found in the grains. The parallelism of these precipitates indicates that they are following preferred planes in each grain. In this diffused area the MgO particles appear to have a formation around them which is slightly lighter than the particles themselves. Correlating this observation with the results of the X-ray diffraction study points to the following interpretation. The X-ray diffraction data showed the presence of chromium, Cr_2N , and MgCr_2O_4 in the diffused area. From the photomicrographs the chromium appears to be the matrix material, the MgCr_2O_4 spinel is shown by the large gray areas around the small dark MgO inclusions, and the Cr_2N is in the grain boundaries as well as in the lamellar precipitates within the grains. Nitrides are known to form in various materials as straight needle-like

structures. Furthermore, it is known that chromium is a known acceptor of nitrogen from the air in large quantities as the temperature is increased above 2200° F. In fact, the solubility of nitrogen in chromium is given in reference 4 to be 0.2 percent by weight at 2400° F. A wet chemical analysis by the W. B. Coleman Co. of Philadelphia on the as-received Cr-MgO composite used in this investigation showed 0.009-percent nitrogen. Material oxidized for 4 hours at 2500° F was found to contain 4.20-percent nitrogen. Because 4.20 percent is above the solubility limit of nitrogen in chromium, the excess nitrogen precipitates as Cr₂N.

Electron micrographs of the Cr-MgO composite were made to complement the light micrographs. Figure 21 shows a magnesium oxide inclusion in the as-received composite material. The dark areas on the MgO inclusions may be magnesite (MgCO₃). Magnesium oxide is produced from magnesite by methods described in reference 5, and the dark areas in figure 21 indicate that transformation to MgO may not have been complete. Figure 22 shows an enlargement of one of these dark areas and the structure appears to be very porous. An electron micrograph showing a similar porous structure appears in figure 4 of reference 6; in this reference the structure is identified as magnesite.

Hardness measurements.- Hardness measurements are shown in figure 23 for an as-received specimen and for one that was oxidized at 2500° F for 4 hours. The as-received material shows a uniform Knoop hardness of 200 whereas the exposed specimen has an extremely hard layer (Knoop hardness of 1,190) near the surface and a Knoop hardness of 280 near the center of the specimen. All hardness measurements were taken in the matrix and the high Knoop hardness at the surface of the exposed specimen confirms the nitrogen penetration into the Cr-MgO material as detected by the X-ray diffraction techniques.

Fabrication

The fabrication characteristics of the Cr-MgO composite were studied by the machining and testing of threaded fasteners plus the forming and welding of the sheet material. Several bolts and nuts like the one shown in figure 24 were machined from the 5/8-inch-diameter bar stock and were oxidized at various temperatures from 2000° F to 2600° F to determine the feasibility of using this material for threaded fasteners that would be exposed to elevated temperatures. Some of the bolts and nuts were assembled after coating the threads with a slurry of MgO + H₂O as recommended by the developers of the material. This procedure was reported to be helpful in alleviating seizure of the bolt and nut assembly. After exposing these assemblies at temperatures of 2000° F to 2600° F an attempt was made to remove the nuts from the coated as well as from the uncoated bolts. All bolts failed in shear on attempted disassembly. Similar results are reported in reference 7. The nut and bolt assemblies were sectioned to determine why the nuts had seized. Figure 25 shows the microstructure in the region of the threads. There is a diffused zone on the left side of the figure, and the threads on the right are virtually welded together. This condition indicates that solid-state diffusion bonding of the material may have occurred.

Other fabrication experiences with this material include cutting, hot forming, and electron-beam welding of the sheet material in the preparation of the specimen shown in figure 26. It was found that cutting the sheet could best be accomplished

by an electrical discharge cutting machine. The forming of the curved nose piece and the rolling of the two circular half sections for the cylindrical body were accomplished with relative ease at 1000° F. Electron beam welding of the specimens was accomplished after experimental determination of the welding parameters. Inspection of the weld revealed that it was only of fair quality. It was believed that this lack of quality was due to the evaporation of the Cr-MgO material under the vacuum and temperature conditions required to effect the weld. This belief was corroborated by two subsequent tests in a vacuum furnace at 2500° F for 1 hour. The pressure in the furnace was 2×10^{-4} mm Hg, and both specimens showed a weight loss of approximately 10 percent. This loss is considered to be excessive and would impair the weldability. Spot-welding of the Cr-MgO sheet was accomplished with very light pressure and satisfactory results were obtained.

SUMMARY OF RESULTS

An integrated mechanical property and metallurgical study was made on a metallic chromium and magnesium oxide composite to determine its capabilities and limitations as a structural material for elevated-temperature applications. The following results are based on this investigation:

1. The Cr-MgO composite material tested in this investigation had room-temperature tensile and yield strengths of 40 and 33 ksi, respectively. Pre-oxidation at 2000° F did not affect the strength, but preoxidizing the Cr-MgO at 2200° F and higher caused a loss in room-temperature strength.
2. The elevated-temperature strength of the Cr-MgO composite dropped rapidly and at 2000° F the tensile strength was only 25 percent of the room-temperature value. At 2600° F the tensile strength was only 7 percent of the room-temperature strength.
3. The room-temperature elongation of the Cr-MgO composite sheet was found to be 3 percent. The elongation decreased as the Cr-MgO was preoxidized at temperatures of 2000° F and above.
4. The comparison of the Cr-MgO composite sheet with a coated refractory metal sheet on a strength-weight basis indicates that the Cr-MgO composite is not competitive with the coated refractory as a structural material at room or elevated temperatures.
5. The oxidation rates during oxidation tests in static air were found to be rapid above 2200° F, and yttrium additions to the composite did not improve its resistance to oxidation. The oxide film formed on the surface during oxidation was composed of Cr_2O_3 and MgCr_2O_4 and the difference in the thermal expansion of the MgCr_2O_4 and the base material Cr-MgO apparently caused the oxides to spall during cooling. In dynamic oxidation tests in air moving at a high velocity at 3200° F for 5 minutes the material eroded and melted.

6. A metallographic examination of the oxidized specimens showed that a diffused layer penetrated into the base material at a much faster rate than the rate at which the original material was being lost to oxidation. This layer consisted of a supersaturated solution of nitrogen and a precipitate of chromium nitride which were responsible for the embrittling at room temperature after preoxidation.

7. The hardness tests showed a very hard zone (Knoop hardness of 1,190) below the surface of the material that had been exposed to temperatures above 2000° F. This hard zone confirms that chromium nitride was present in the exposed material.

8. Bend tests to determine the bending transition temperature showed this transition temperature to be 85° F. The tension transition temperature, based on elongation measurements from tensile tests, was found to lie between 75° F and 100° F.

9. Fabrication characteristics of the Cr-MgO composite were studied by machining, forming, and joining. Threaded fasteners were tested and all failed on attempted disassembly after heating. Joining of thin sheet by electron beam welding could be accomplished but was hampered by excessive evaporation of the chromium. Sheet material was readily formed into half circles with a bend radius of 5/8 inch at 1000° F.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., February 25, 1963.

REFERENCES

1. Scruggs, David M.: Modified Chromium for Unprotected Structures Over 2600° F. [Preprint] 1688-61, American Rocket Soc., Apr. 1961.
2. Kotanchik, Joseph N., and Ross, Robert D.: Electric Arc-Powered Research Facilities for Materials and Structures Testing. Presented at annual winter meeting of American Soc. Mech. Eng. (New York, N.Y.), Nov. 26 - Dec. 1, 1961.
3. Mathauser, Eldon E., Stein, Bland A., and Rummler, Donald R.: Investigation of Problems Associated With the Use of Alloyed Molybdenum Sheet in Structures at Elevated Temperatures. NASA TN D-447, 1960.
4. Clauer, A. H., and Maringer, R. E.: The Effects of Interstitials on the Internal Friction of Chromium. Contract No. AF 33(616)-5080, Battelle Memorial Inst., Mar. 14, 1962.
5. Kingery, W. D.: Introduction to Ceramics. John Wiley & Sons, Inc., c.1960.
6. Pende, A., and Singh, Rabindar: Electron Microscope and Electron Diffraction Studies of Sintering of Magnesite. Jour. American Ceramic Soc., vol. 41, no. 10, Oct. 1958, pp. 394-397.
7. Marr, F. G.: Evaluation of Cerametalix Threaded Fasteners. Rep. No. DS-SR-032 MP, Boeing Airplane Co., Sept. 29, 1961.

TABLE I.- ROOM-TEMPERATURE TENSILE DATA ON

Cr-MgO COMPOSITE SHEET MATERIAL

Material condition	Grain direction	Yield strength, psi	Ultimate strength, psi	Modulus of elasticity, psi	Elongation in 1/2 inch, percent
As received	Longitudinal	33,200	40,500	36.0 × 10 ⁶	2.5
As received	Longitudinal	34,000	40,600	37.0	3.0
As received	Longitudinal	-----	38,000	-----	2.5
As received	Longitudinal	-----	41,800	-----	2.0
As received	Transverse	33,800	36,000	35.4	3.5
As received	Transverse	31,000	32,000	34.8	---
Oxidized* at 2000° F	Longitudinal	33,400	39,800	35.0	1.5
Oxidized* at 2000° F	Longitudinal	-----	40,700	-----	1.0
Oxidized* at 2000° F	Transverse	33,000	40,100	35.4	---
Oxidized* at 2200° F	Longitudinal	26,000	28,800	33.2	.5
Oxidized* at 2200° F	Transverse	26,000	27,000	33.1	.5
Oxidized* at 2200° F	Transverse	-----	27,500	-----	.5

*Oxidized 1 hour.

TABLE II.- ELEVATED-TEMPERATURE TENSILE DATA ON Cr-MgO

AS-RECEIVED SHEET MATERIAL

Temperature, °F	Yield strength, psi	Ultimate strength, psi	Elongation in 1 inch, percent
2,000	6,500	9,800	8.0
2,300	2,840	5,100	8.5
2,600	1,600	2,850	8.5

TABLE III.- LOW-TEMPERATURE TENSILE DATA ON

AS-RECEIVED Cr-MgO BAR STOCK

Temperature, °R	Yield strength, psi	Ultimate strength, psi	Elongation in 1/2 inch, percent
32	31,800	48,000	3.1
85	29,500	47,000	4.5
112	28,300	48,000	9.2

TABLE IV.- X-RAY DIFFRACTION DATA FOR AS-RECEIVED
Cr-MgO COMPOSITE SHEET MATERIAL

Scanning angle, 2θ, deg (*)	d-spacing, A (*)	d-spacing on ASTM MgO card, A	d-spacing on ASTM Cr card, A	Reflecting plane
42.90	2.1063	2.106		200
44.36	2.0390		2.039	110
62.25	1.4898	1.489		220
64.60	1.4415		1.4419	200
81.70	1.1776		1.1774	211
115.20	.91226		.91202	310
115.59	.91025		.91202	310

*From Braggs law:

$$n\lambda = 2d \sin \theta$$

where

λ X-ray wavelength

d distance between successive parallel lattice planes

θ half the scanning angle

n assumed to be 1

TABLE V.- X-RAY DIFFRACTION DATA FOR OXIDE FILM FORMED
ON Cr-MgO COMPOSITE

Scanning angle, 2θ, deg	d-spacing, A (*)	d-spacing on ASTM MgCr ₂ O ₄ card, A	d-spacing on ASTM Cr ₂ O ₃ card, A	Reflecting plane
18.40	4.8176	4.813		111
24.50	3.6302		3.633	012
30.30	2.9472	2.945		220
33.65	2.6608		2.666	104
35.65	2.5163	2.512		311
36.20	2.4793		2.480	110
41.50	2.1741		2.176	113
43.35	2.0850	2.083		400
50.25	1.8137		1.8156	024
54.93	1.670		1.672	116
57.40	1.6039	1.603		511
58.40	1.5788		1.579	122
63.00	1.4742	1.4731		440
64.20	1.4295		1.431	300
71.90	1.3120	1.3176		620
75.80	1.2539	1.2563		622
85.50	1.1347		1.123	134
95.36	1.0417	1.0417		800
109.96	.94053		.9462	324
110.60	.9368	.9317		840
118.60	.89579		.8957	310
125.60	.86602		.8658	416
135.20	.8332		.8331	106
137.50	.8264		.8263	330

*From Braggs law: $n\lambda = 2d \sin \theta$

TABLE VI.- X-RAY DIFFRACTION DATA FOR CrMgO COMPOSITE SURFACE

AFTER OXIDE FILM IS REMOVED

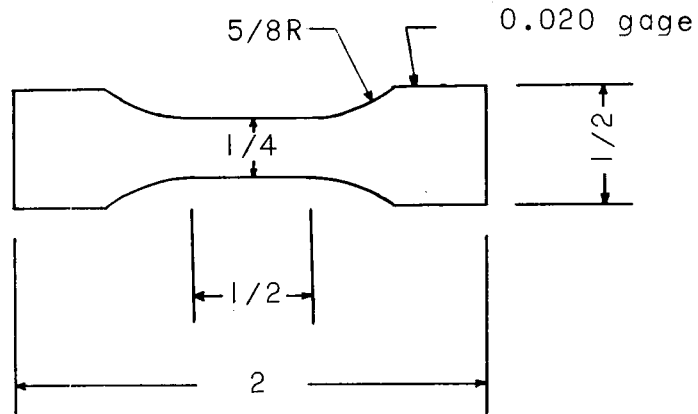
Scanning angle, 2θ , deg	d-spacing, A (*)	d-spacing on ASTM MgCr ₂ O ₄ card, A	d-spacing on ASTM Cr ₂ O ₃ card, A	d-spacing on ASTM β -Cr ₂ N card, A	Reflecting plane
18.35	4.831	4.81	3.633		111
24.50	3.6302		2.666		012
33.60	2.6649				104
35.35	2.528	2.51			311
37.40	2.404	2.406			222
37.50	2.390			2.380	110
42.90	2.108			2.10	111
57.20	1.608	1.603			511
63.60	1.4617		1.465		214
67.70	1.3828		1.1488	1.38	221
83.60	1.1556		.8883		210
121.20	.8841				301

*From Braggs law: $n\lambda = 2d \sin \theta$

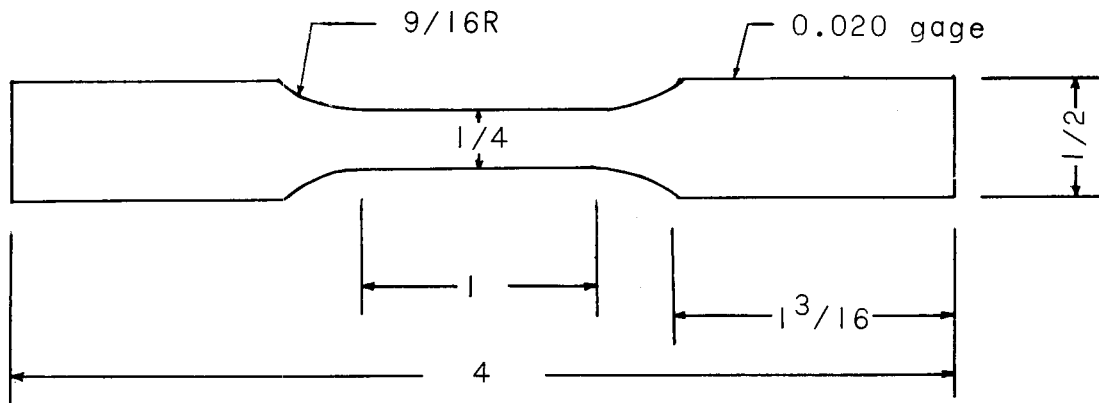
TABLE VII.- X-RAY DIFFRACTION RESULT FOR Cr-MgO COMPOSITE SURFACE
AFTER OXIDE FILM IS REMOVED AND SURFACE CLEANED

Scanning angle, 2θ , deg	d-spacing, A (*)	d-spacing on ASTM MgCr_2O_4 card, A	d-spacing on ASTM Cr card, A	d-spacing on ASTM $\beta\text{-Cr}_2\text{N}$ card, A	Reflecting plane
18.42	4.8125	4.81			111
35.70	2.5128	2.51		2.38	311
37.80	2.3779			2.10	110
43.10	2.0970				111
44.40	2.0386		2.041		
57.30	1.6065	1.603			511
63.00	1.4742	1.473			440
68.20	1.3779			1.380	221

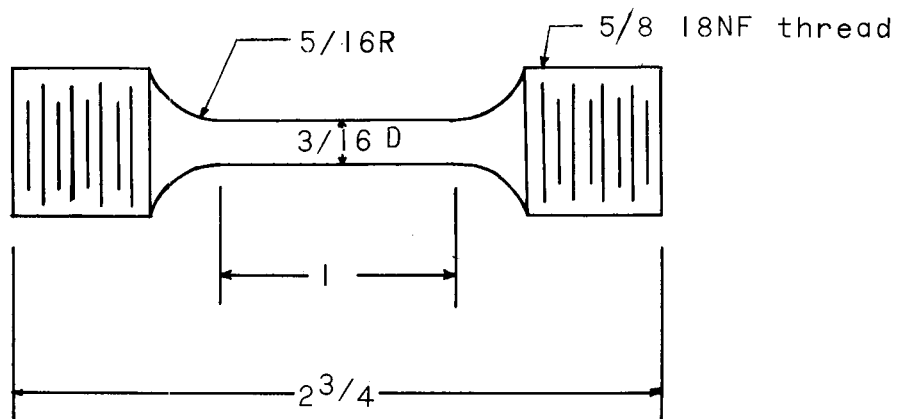
*From Braggs law: $n\lambda = 2d \sin \theta$



(a) Room-temperature sheet tensile specimen.



(b) Elevated-temperature sheet tensile specimen.



(c) Bar tensile specimen.

Figure 1.- Room- and elevated-temperature tensile specimens. All dimensions are in inches.

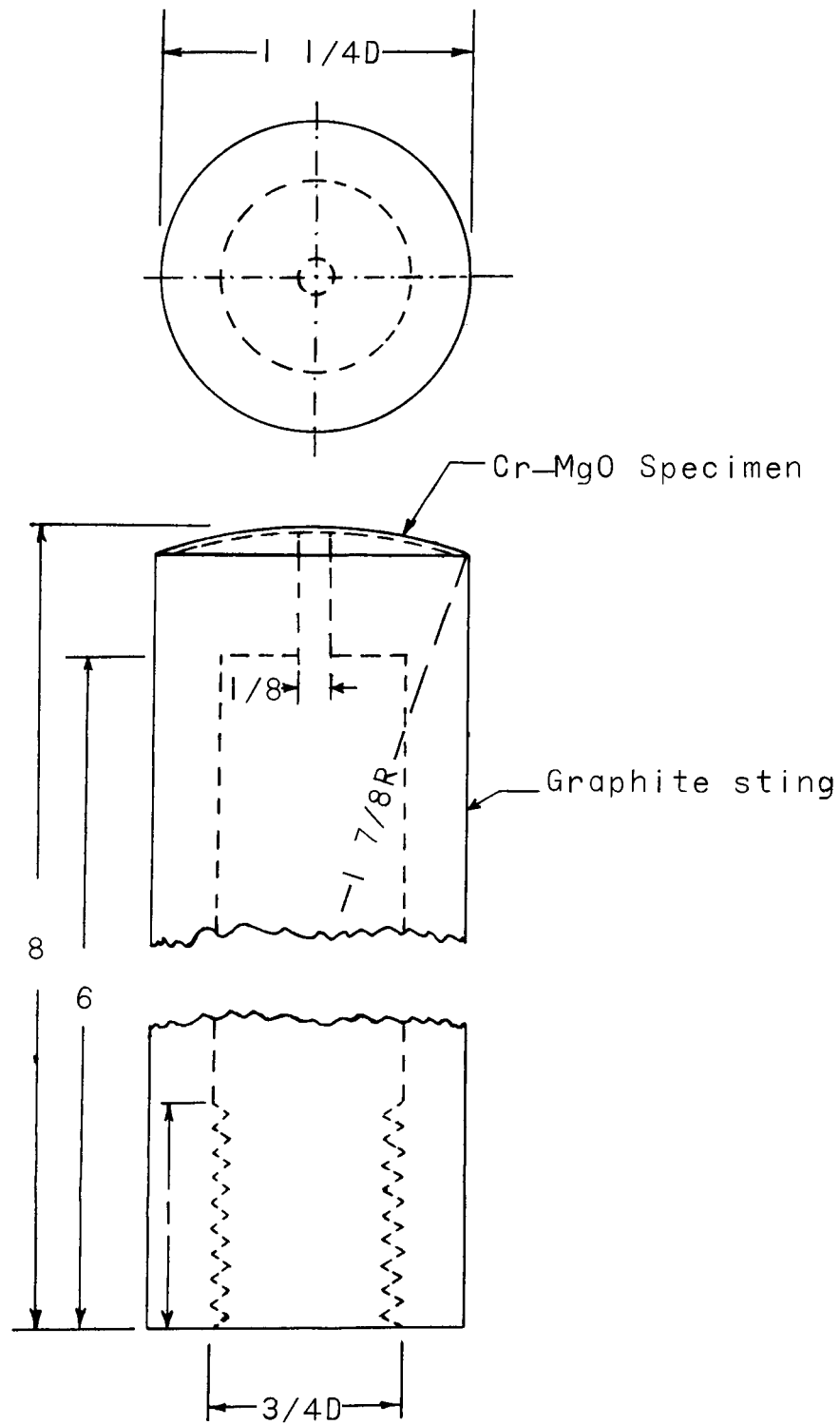


Figure 2.- Cr-MgO composite specimen and graphite sting for dynamic-oxidation tests in 2500-kilowatt arc jet. All dimensions are in inches.

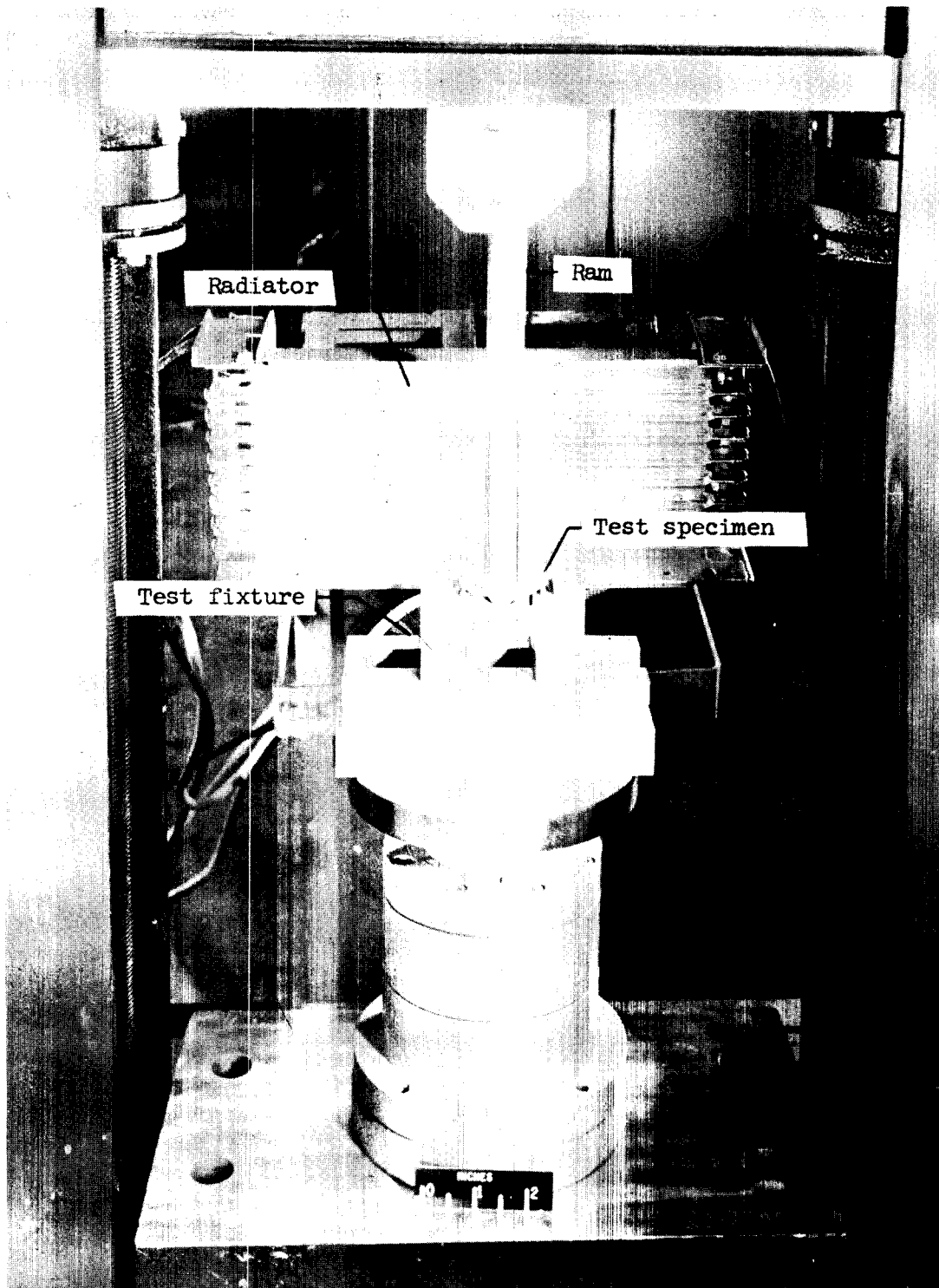


Figure 3.- Test equipment for determining bend transition temperature. One bank of radiators removed. L-63-65

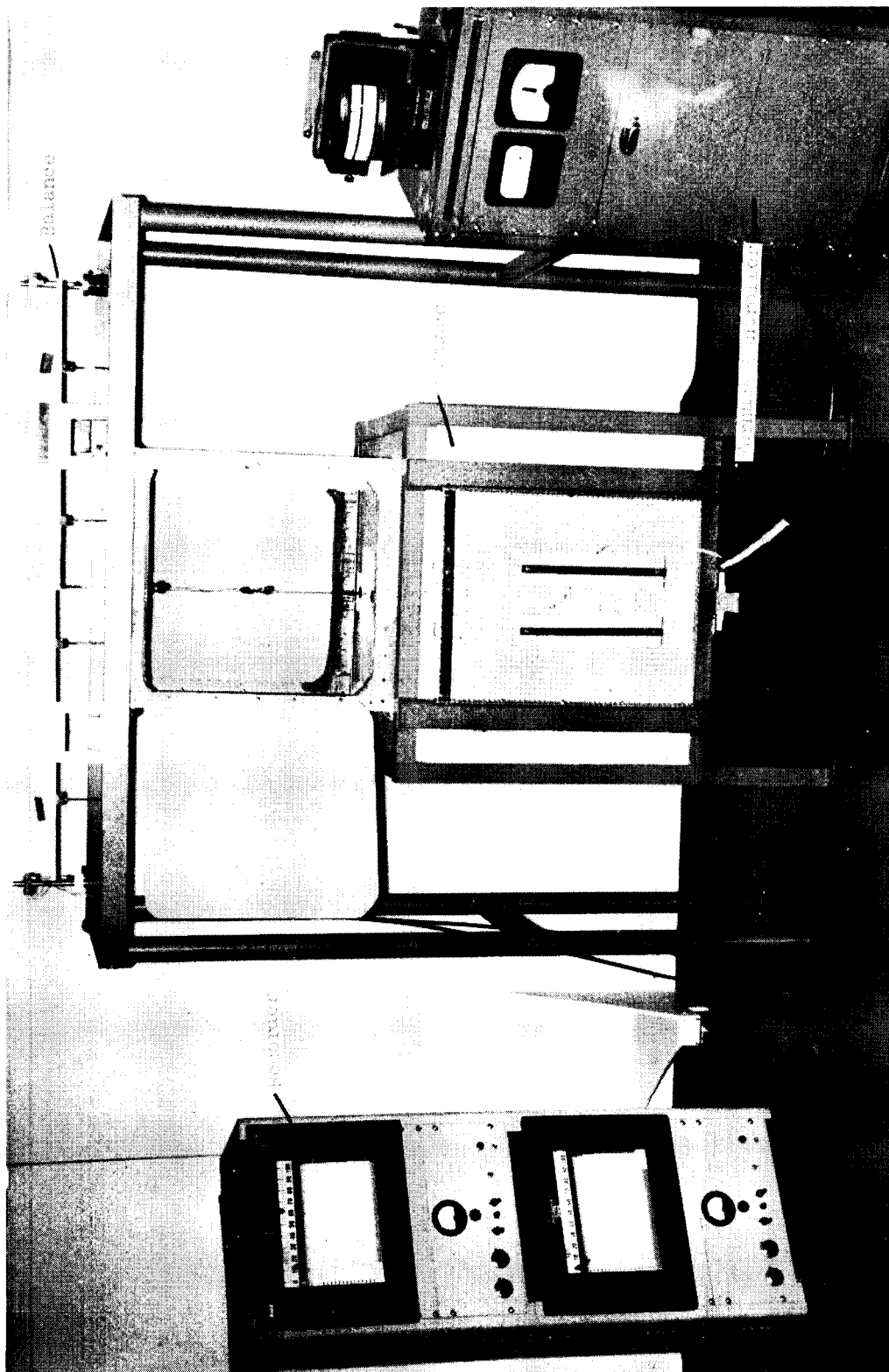


Figure 4.- Balance and furnace setup for making static oxidation tests. L-62-9206.1

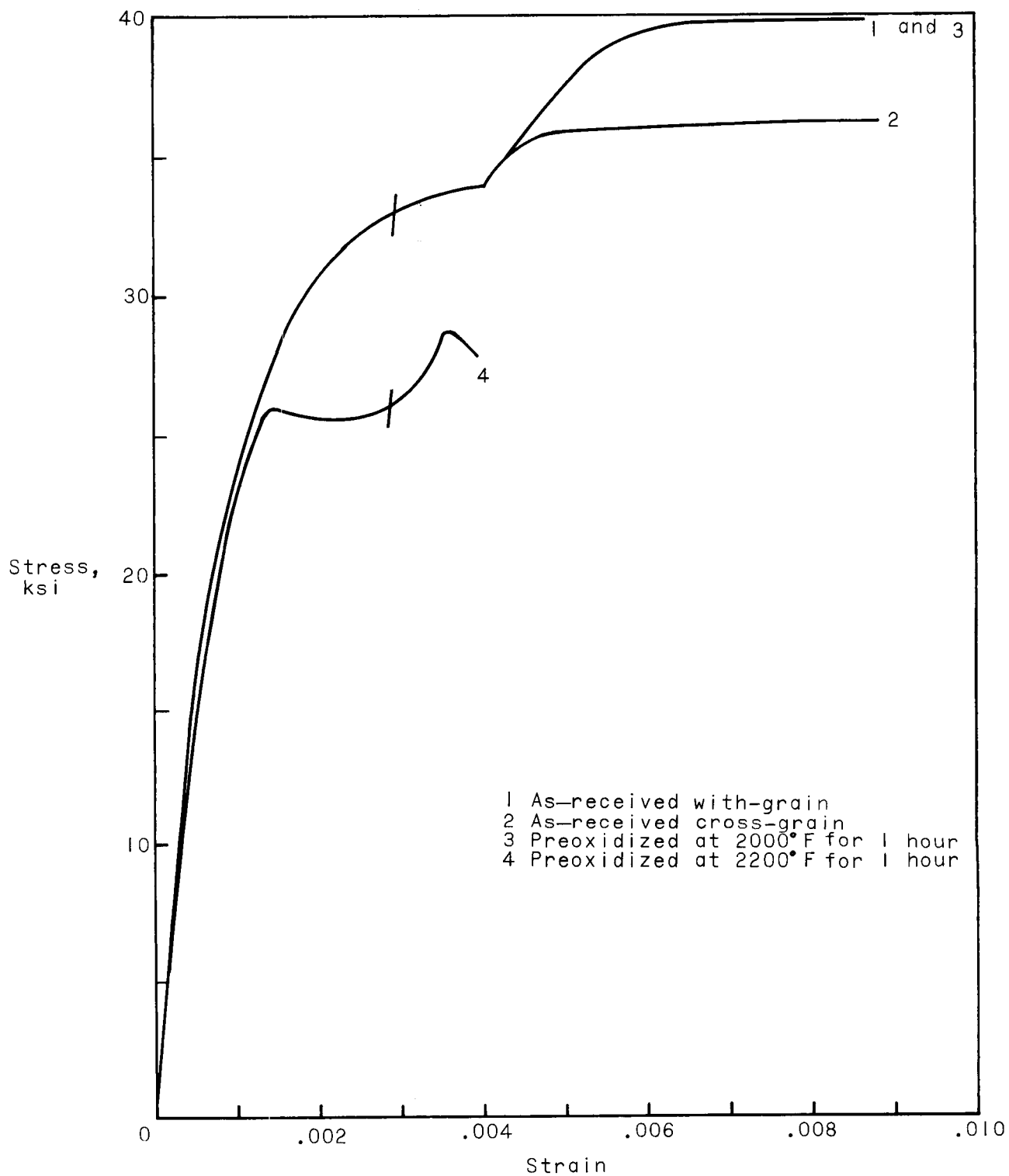


Figure 5.- Tensile stress-strain curves for Cr-MgO composite sheet at room temperature.

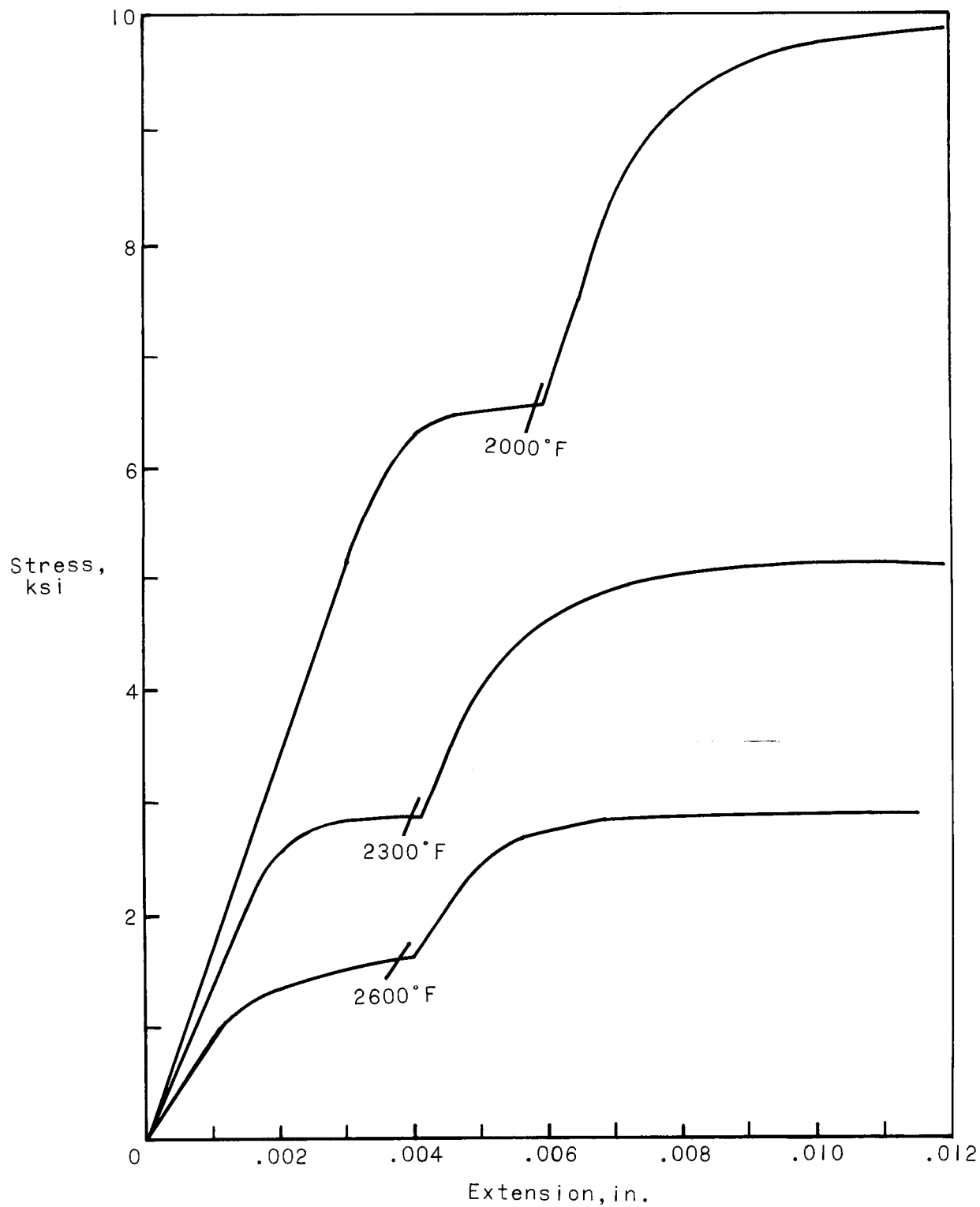


Figure 6.- Stress-extension curves for Cr-MgO composite sheet at elevated temperatures.

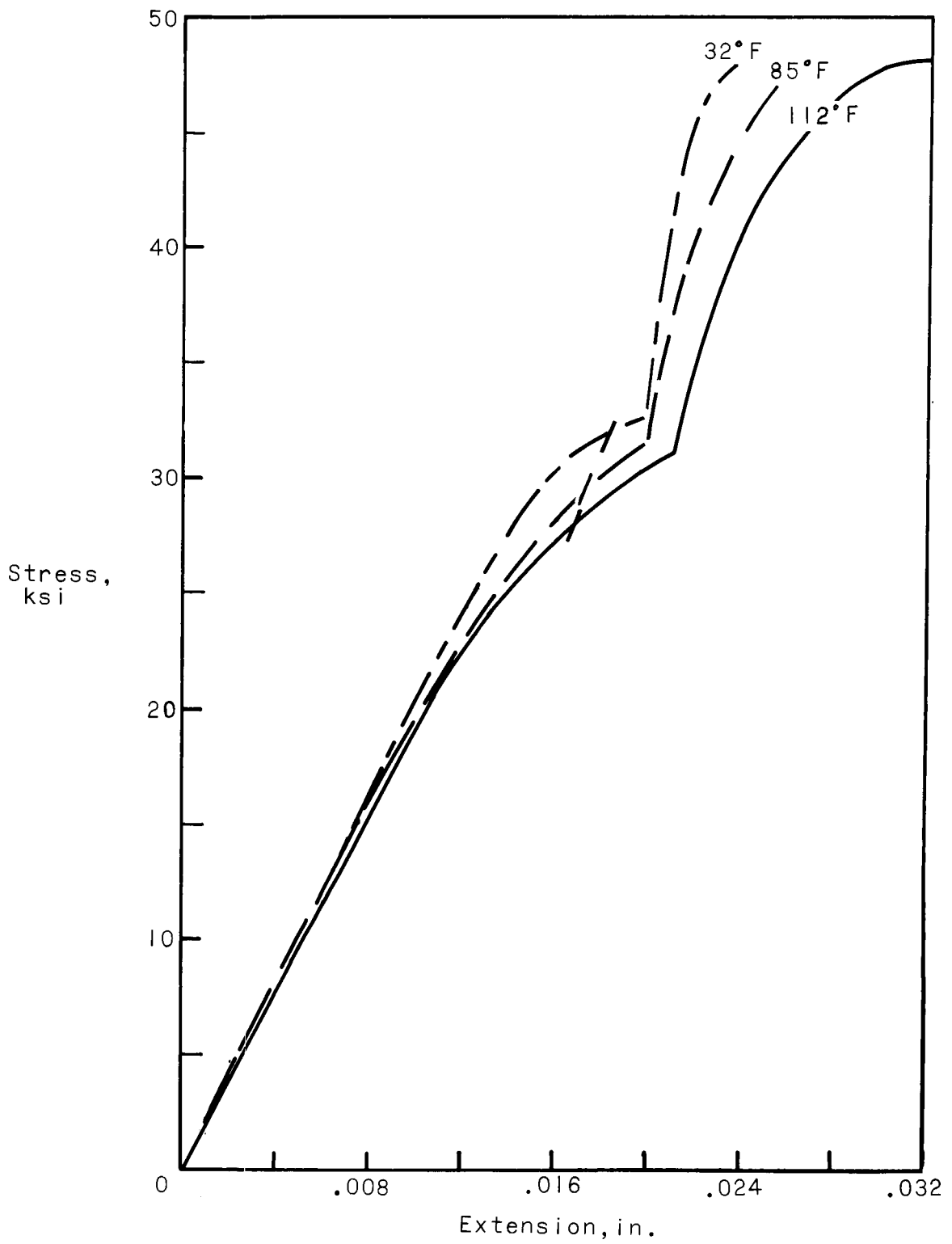


Figure 7.- Stress-extension curves for Cr-MgO composite bar from 32° F to 112° F.

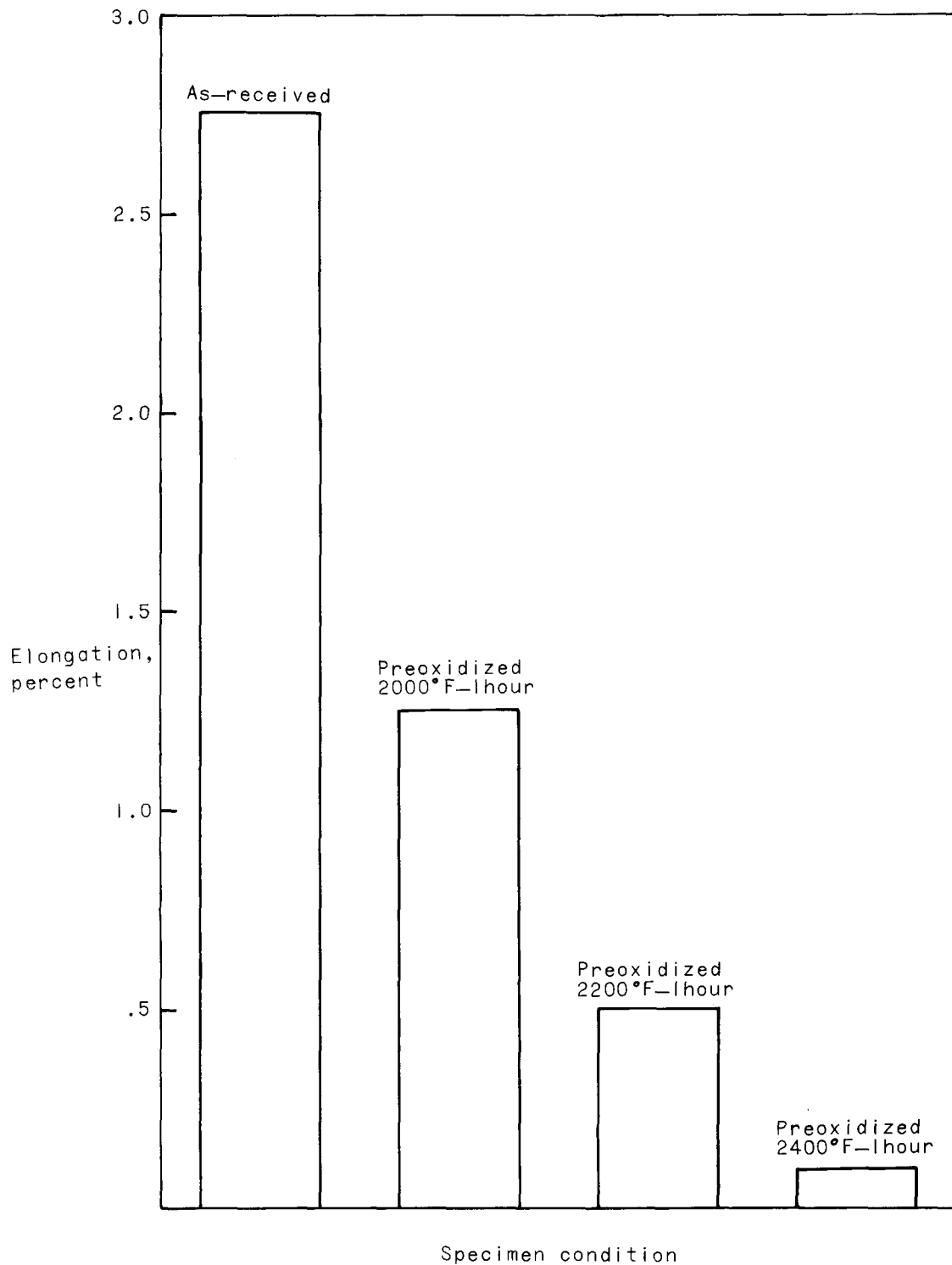


Figure 8.- Room-temperature elongation data for Cr-MgO composite sheet material preoxidized at temperatures ranging from 2000° F to 2400° F.

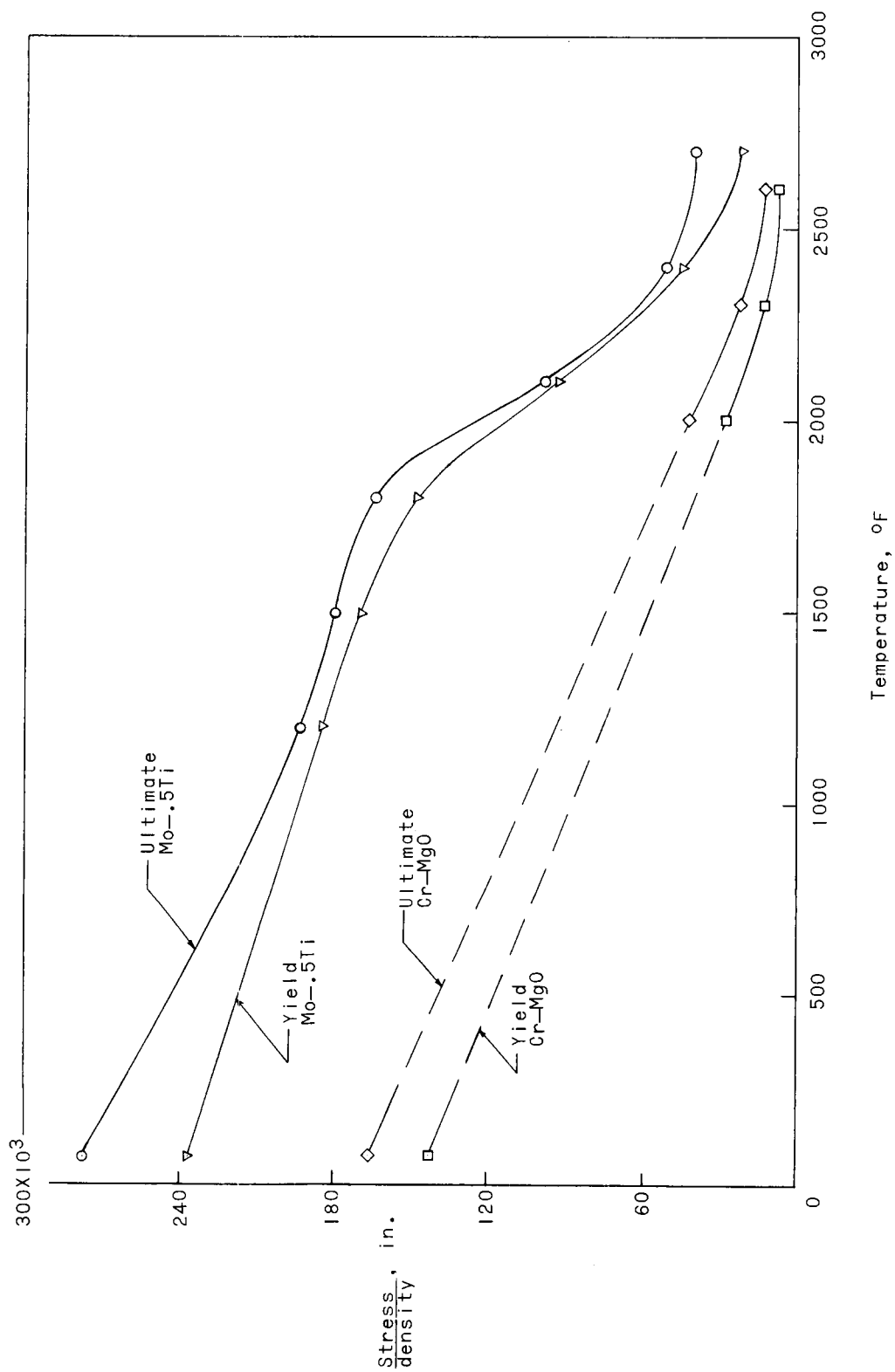


Figure 9.- Comparison of Cr-MgO composite sheet and Mo-.5Ti sheet on a weight-strength basis for temperatures ranging from 100° F to 2600° F.

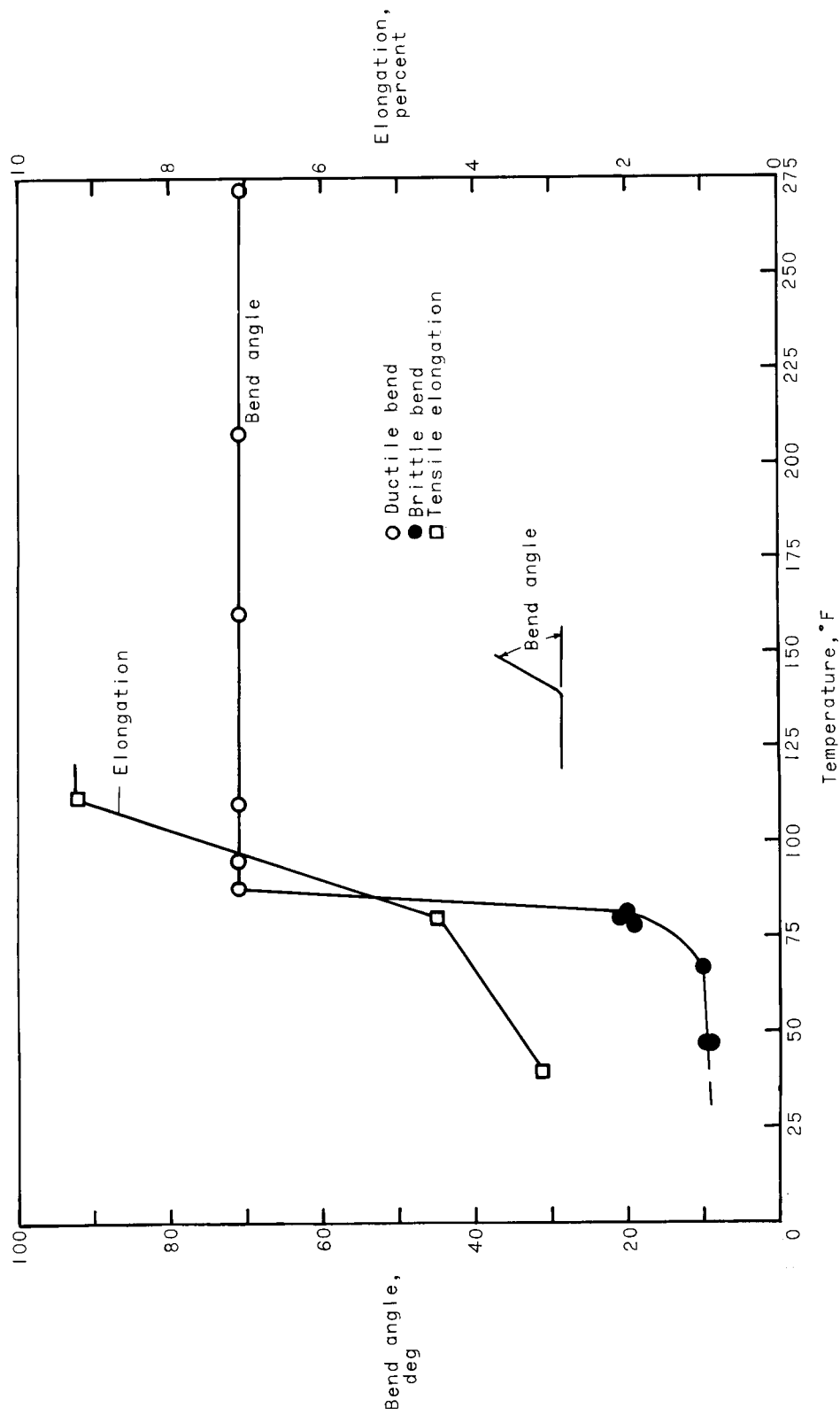


Figure 10.- Curves showing brittle to ductile transition in bending and tension.

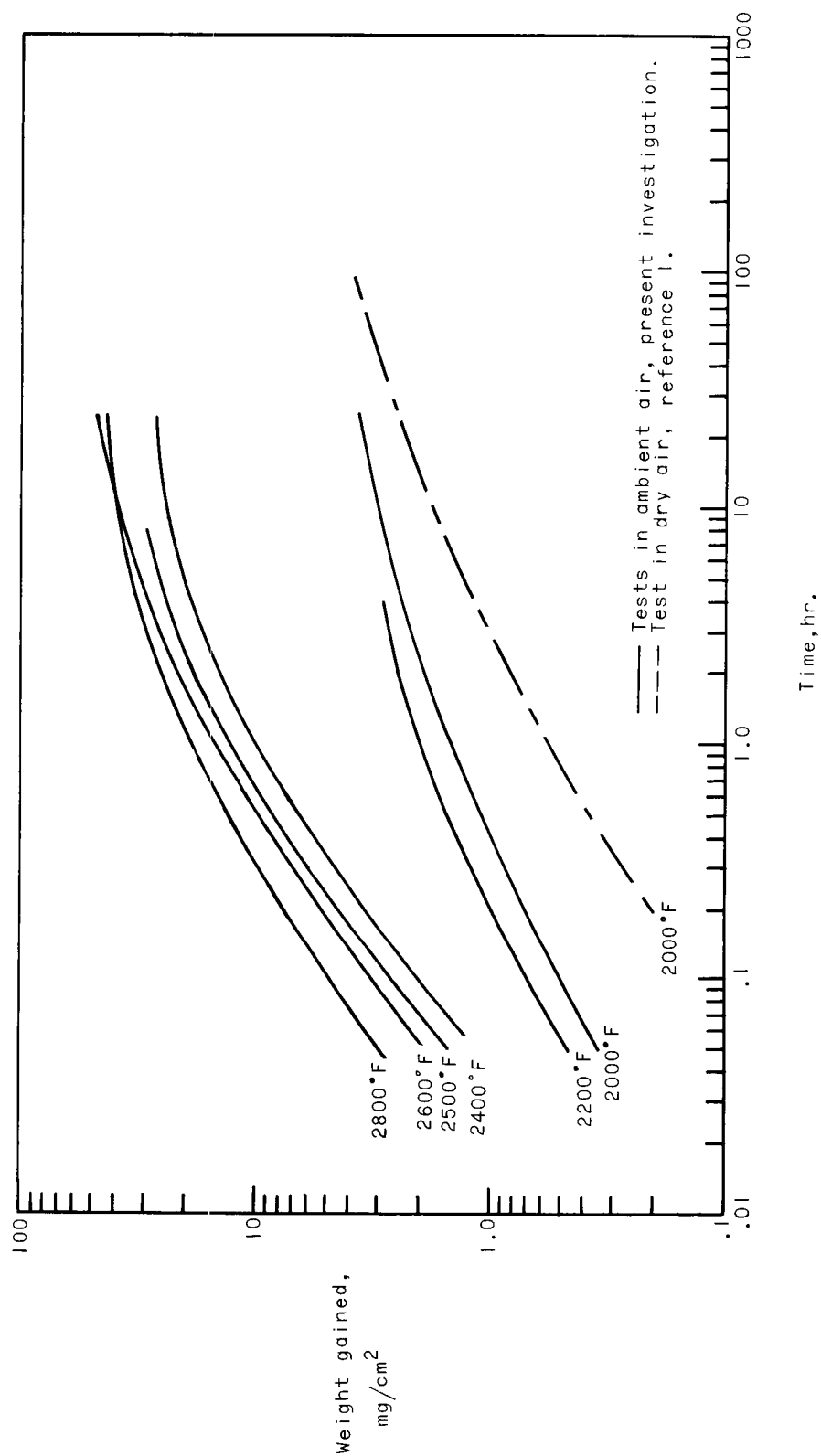


Figure 11.- Oxidation curves for the Cr-MgO composite showing variation of weight gain with time.

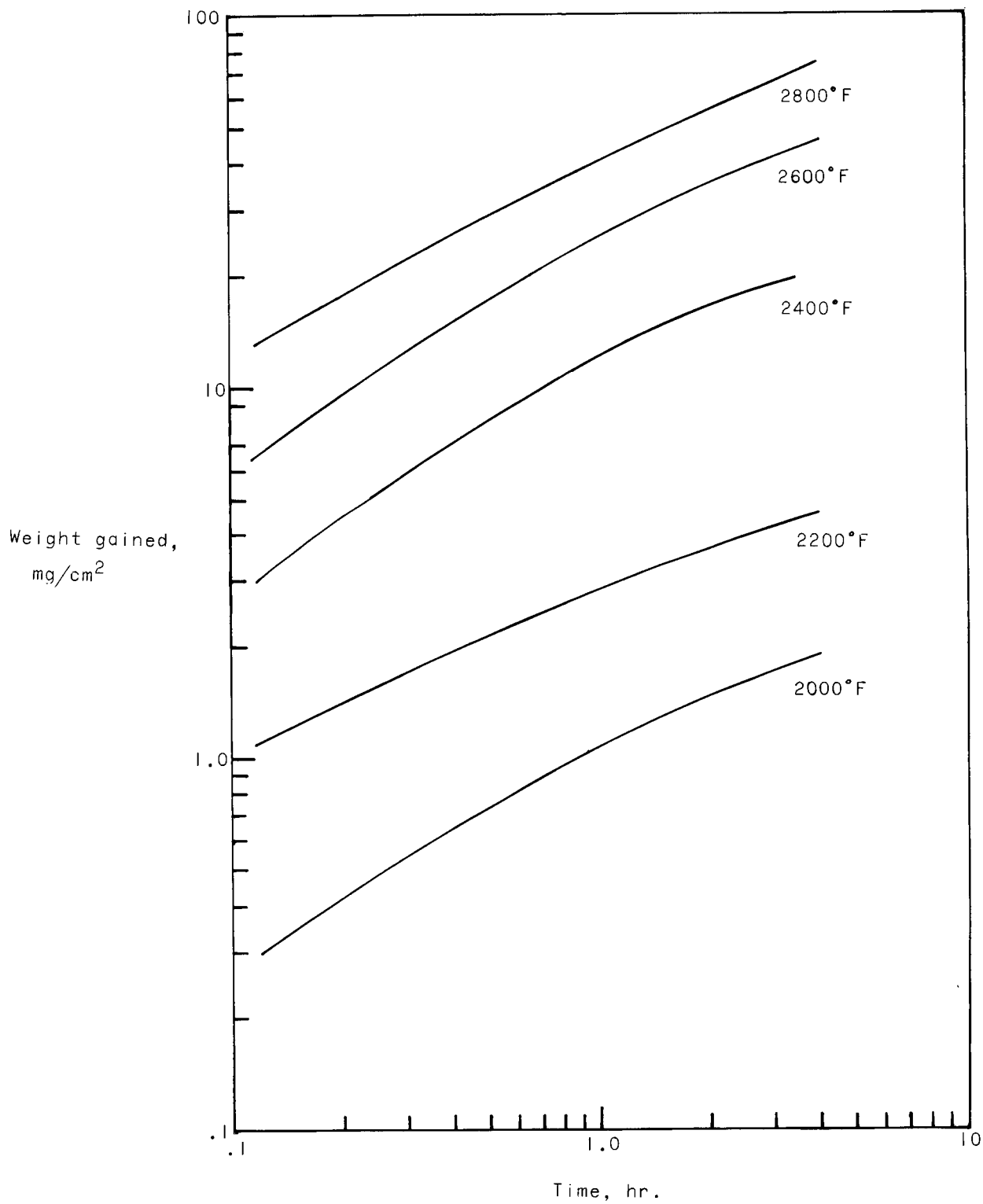


Figure 12.- Oxidation curves for Cr-MgO composite plus yttrium showing weight gain plotted against time.

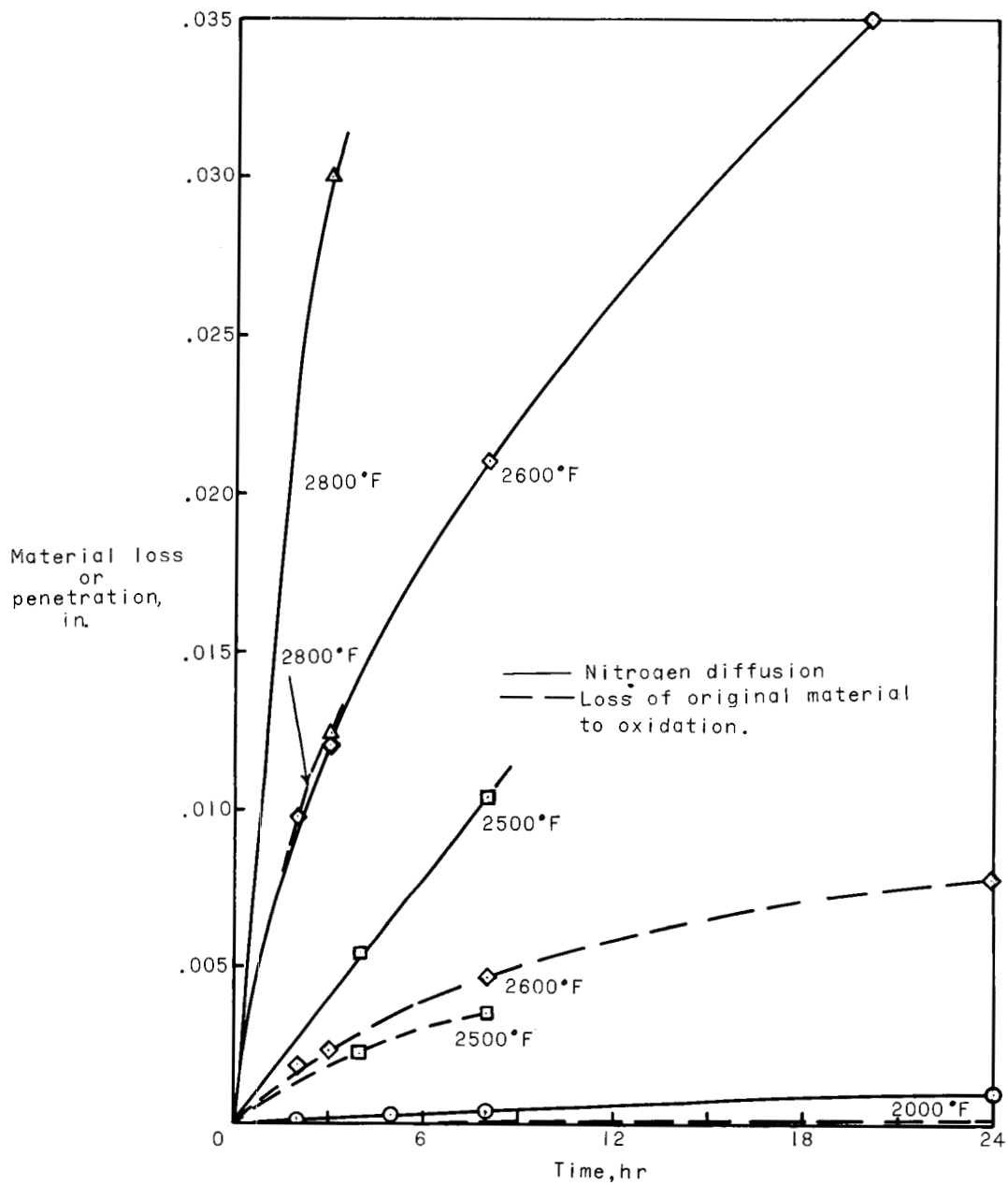


Figure 13.- Curves for material loss or diffused layer plotted against time for Cr-MgO composite for sheet and rod material.

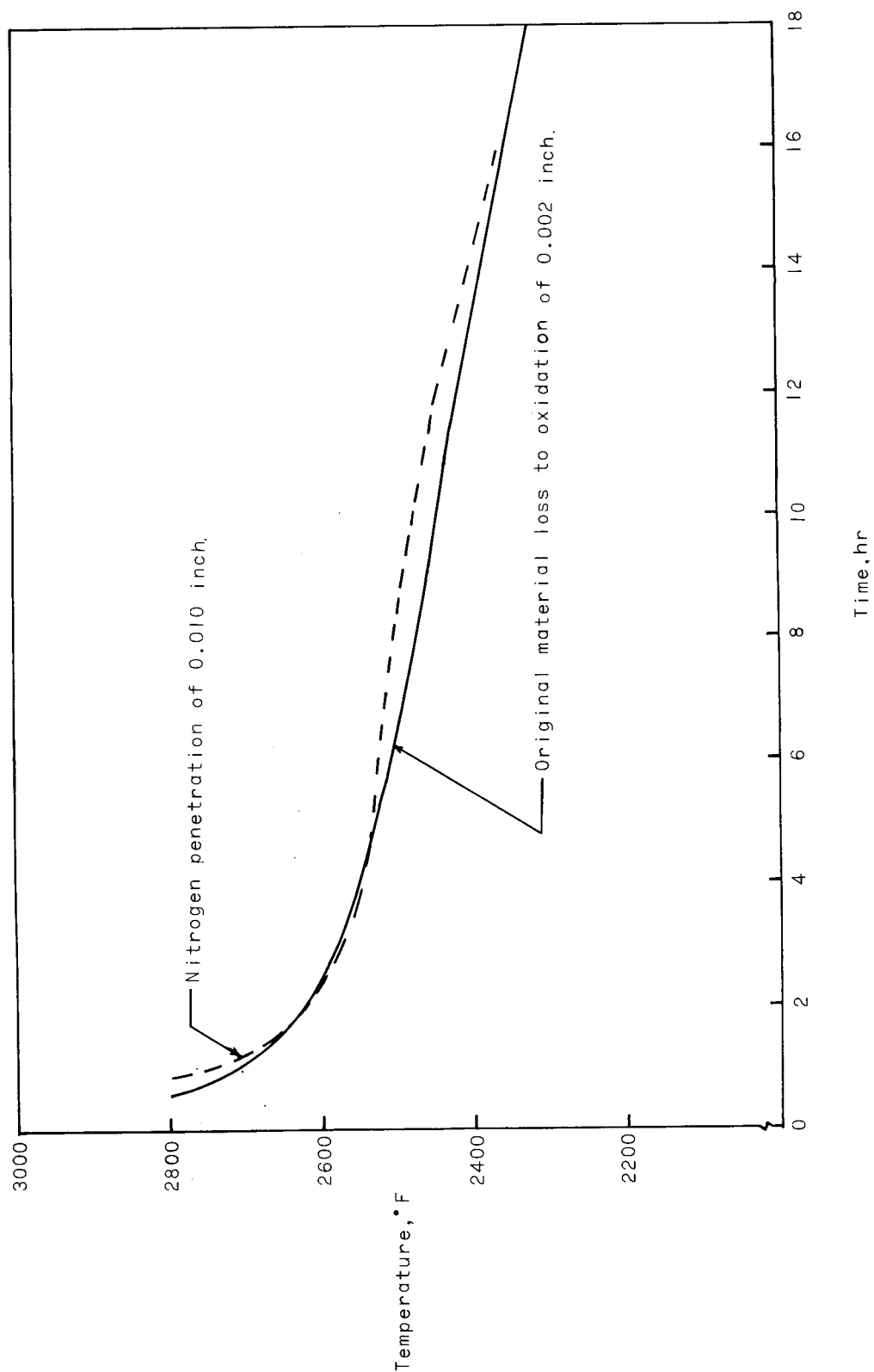
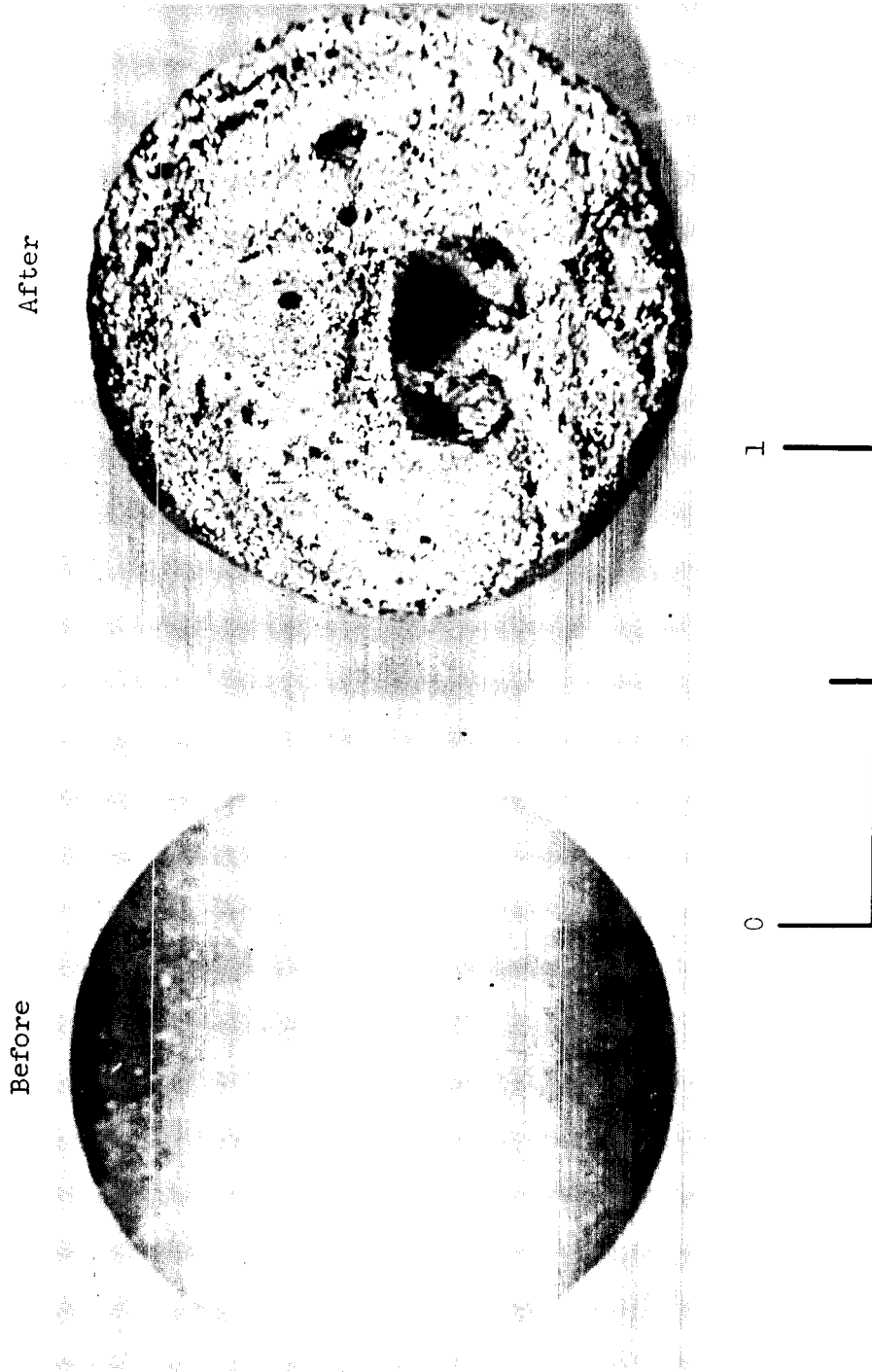
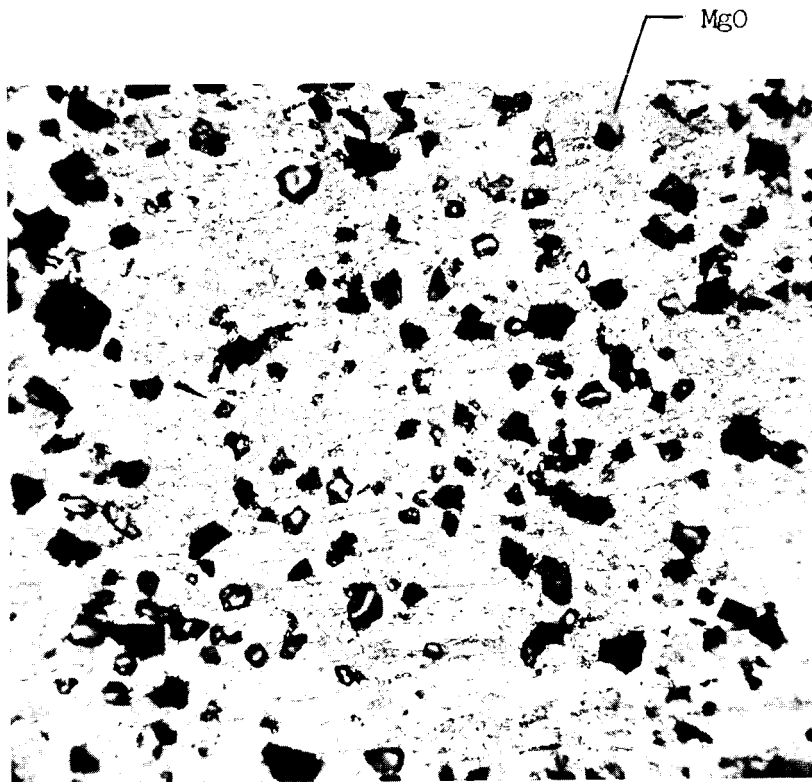


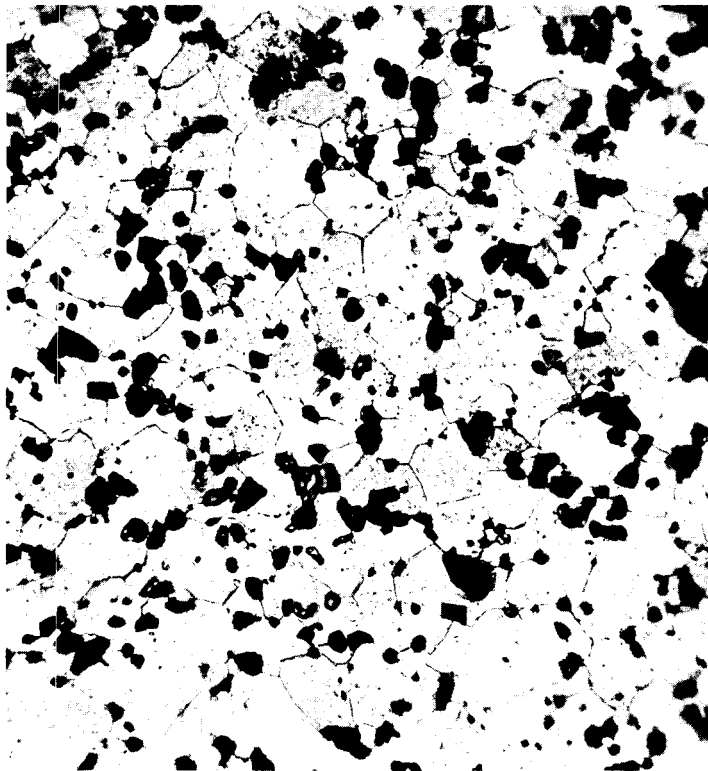
Figure 14.- Temperature-time curves showing 0.002-inch loss of material to oxidation and 0.010 inch of material to nitrogen penetration on 0.020-inch-thick sheet.



L-63-66
Figure 15.- Dynamic-oxidation specimen before and after testing in 400-foot-per-second airstream for 5 minutes at 3200° F.
(Scale indicates inches.)



I-63-67
Figure 16.- Microstructure of the Cr-MgO composite sheet in the as-received condition. $\times 500$.



L-63-68
Figure 17.- Microstructure of as-received Cr-MgO composite plus yttrium bar stock. x500.

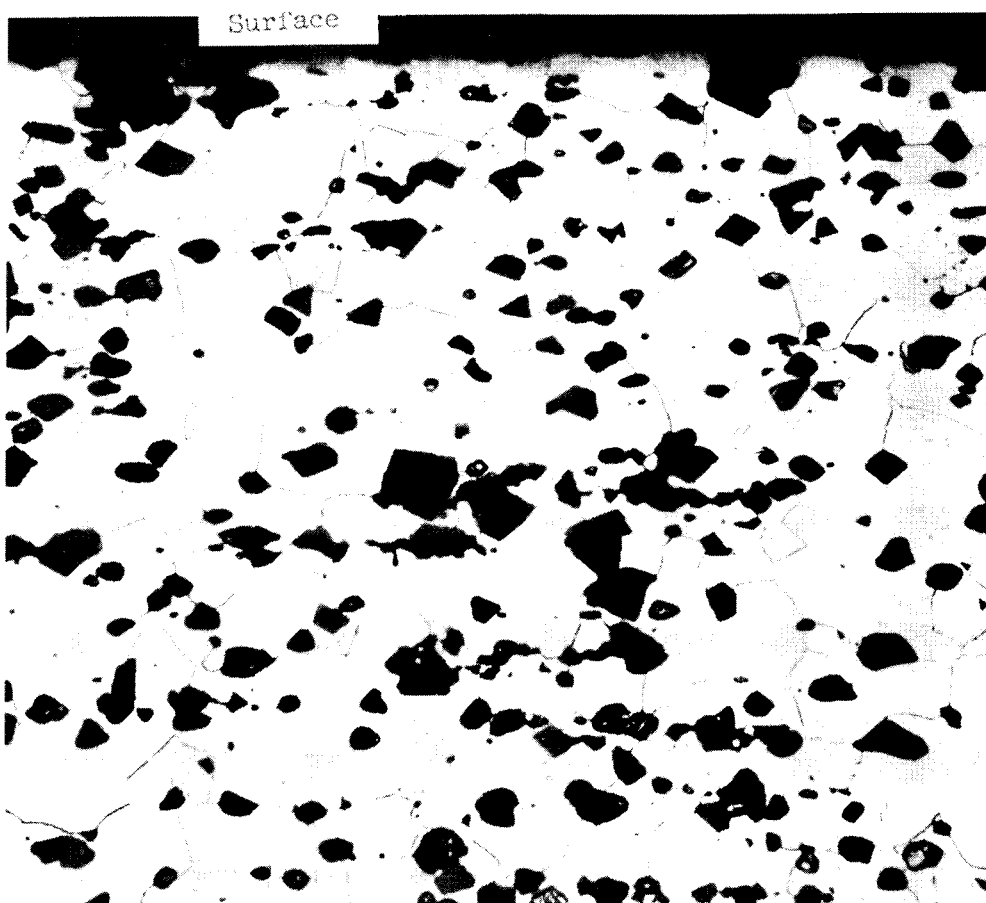
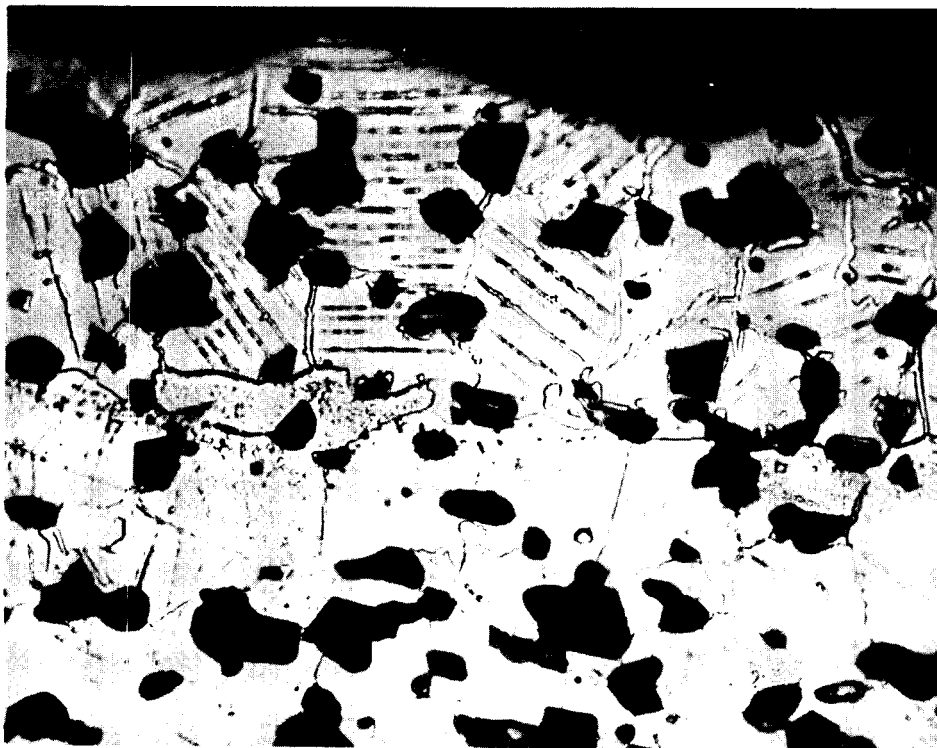


Figure 18.- Microstructure of Cr-MgO composite sheet, after exposure for 4 hours at 2000° F in air. Transverse section. x500. L-63-3161

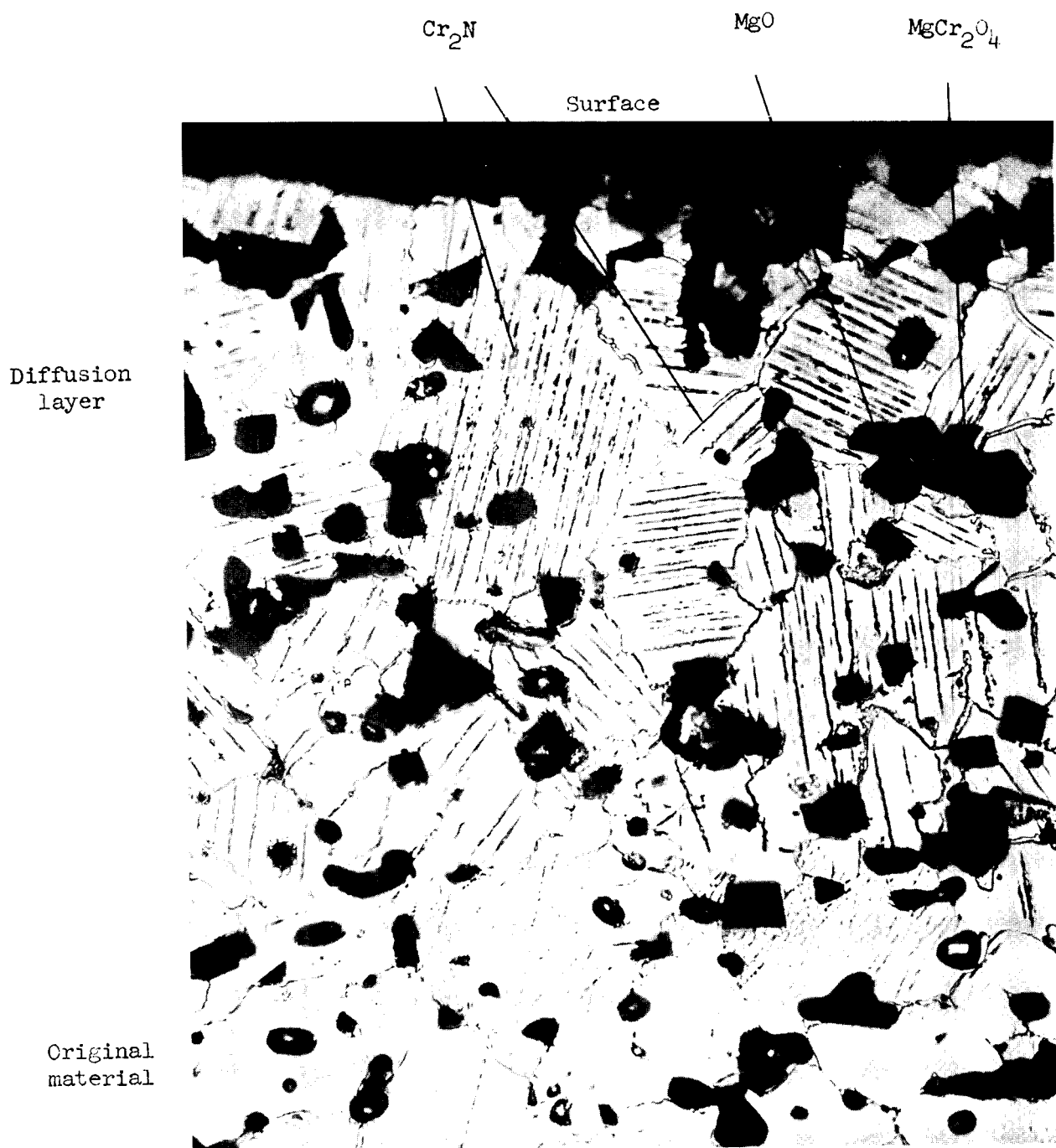
Diffused
layer

Original
material



L-63-70

Figure 19.- Microstructure of Cr-MgO composite sheet, after exposure for 1 hour at 2500° F in air.
Transverse section. x1000.



L-63-71

Figure 20.- Microstructure of Cr-MgO composite sheet, after exposure of 4 hours at 2500° F in air.
Transverse section. $\times 1000$.

See enlargement
next figure

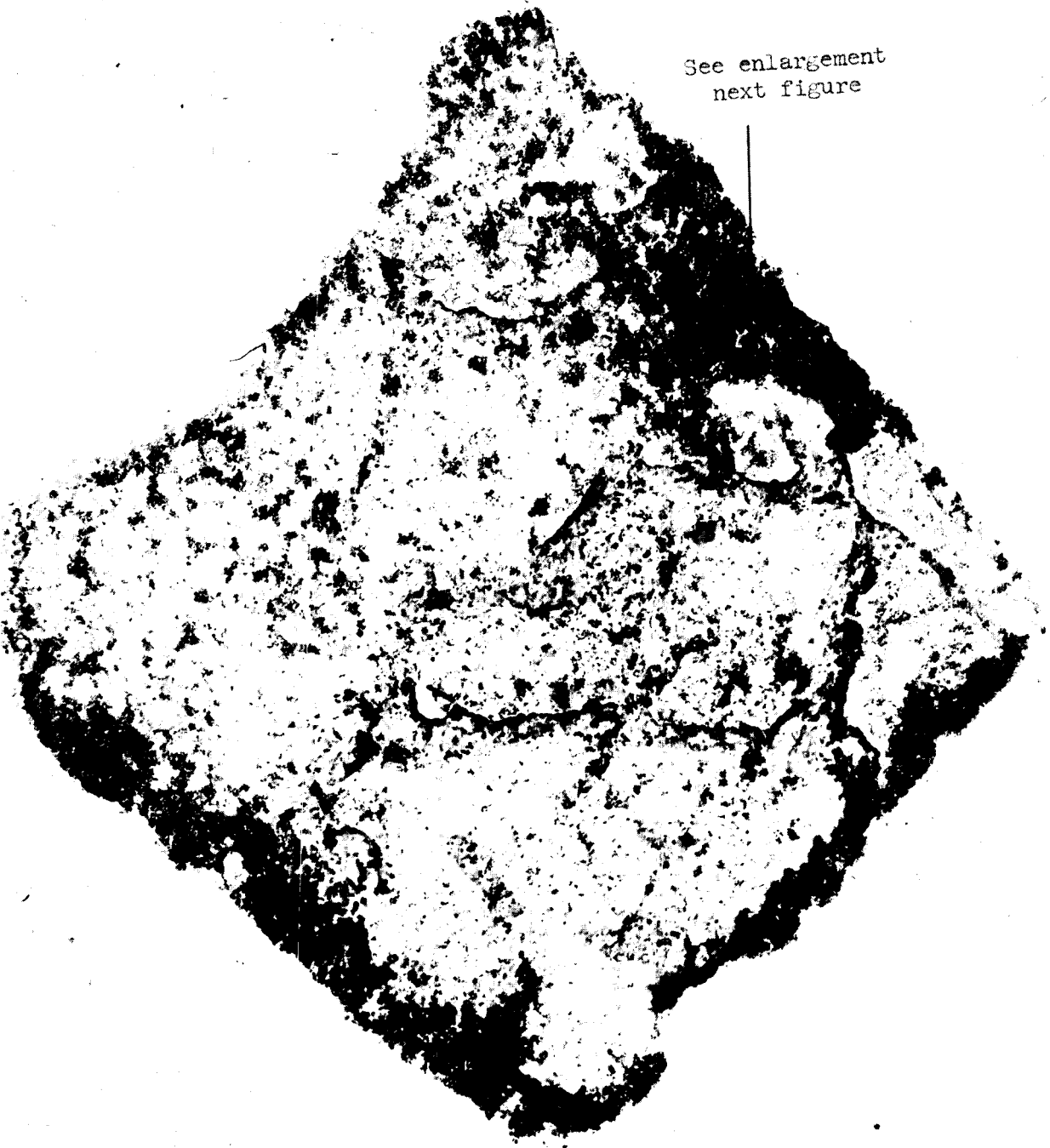
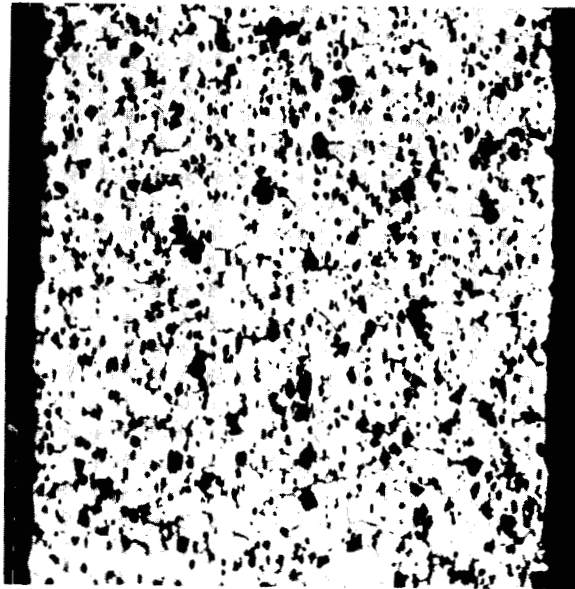


Figure 21.- Electron micrograph of magnesium oxide inclusion in as-received Cr-MgO composite sheet.
x12,500.

L-63-72

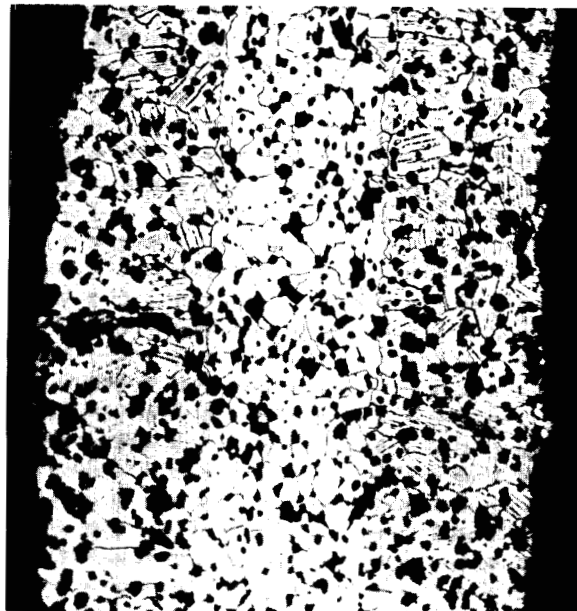


L-63-73
Figure 22.- Electron micrograph showing the porous structure of the dark areas in figure 21. x90,000. Plastic replica used.



200
Knoop

(a) As-received specimen.



1190 280 1190
Knoop Knoop Knoop

(b) Exposed specimen.

L-63-74

Figure 23.- Hardness measurements on as-received Cr-MgO sheet and on an oxidation specimen exposed at 2500° F. Knoop hardness measured with a 100-milligram weight.

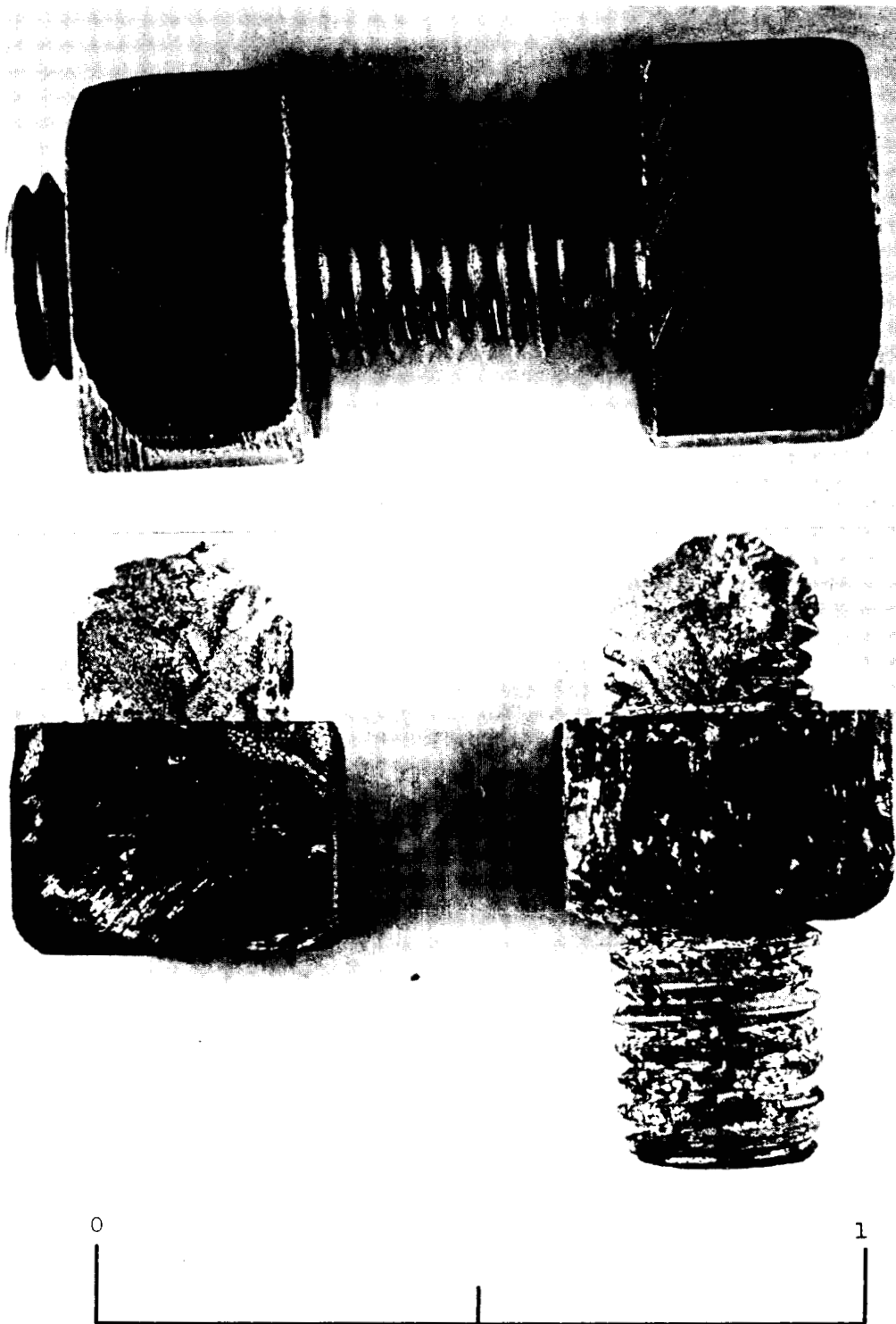
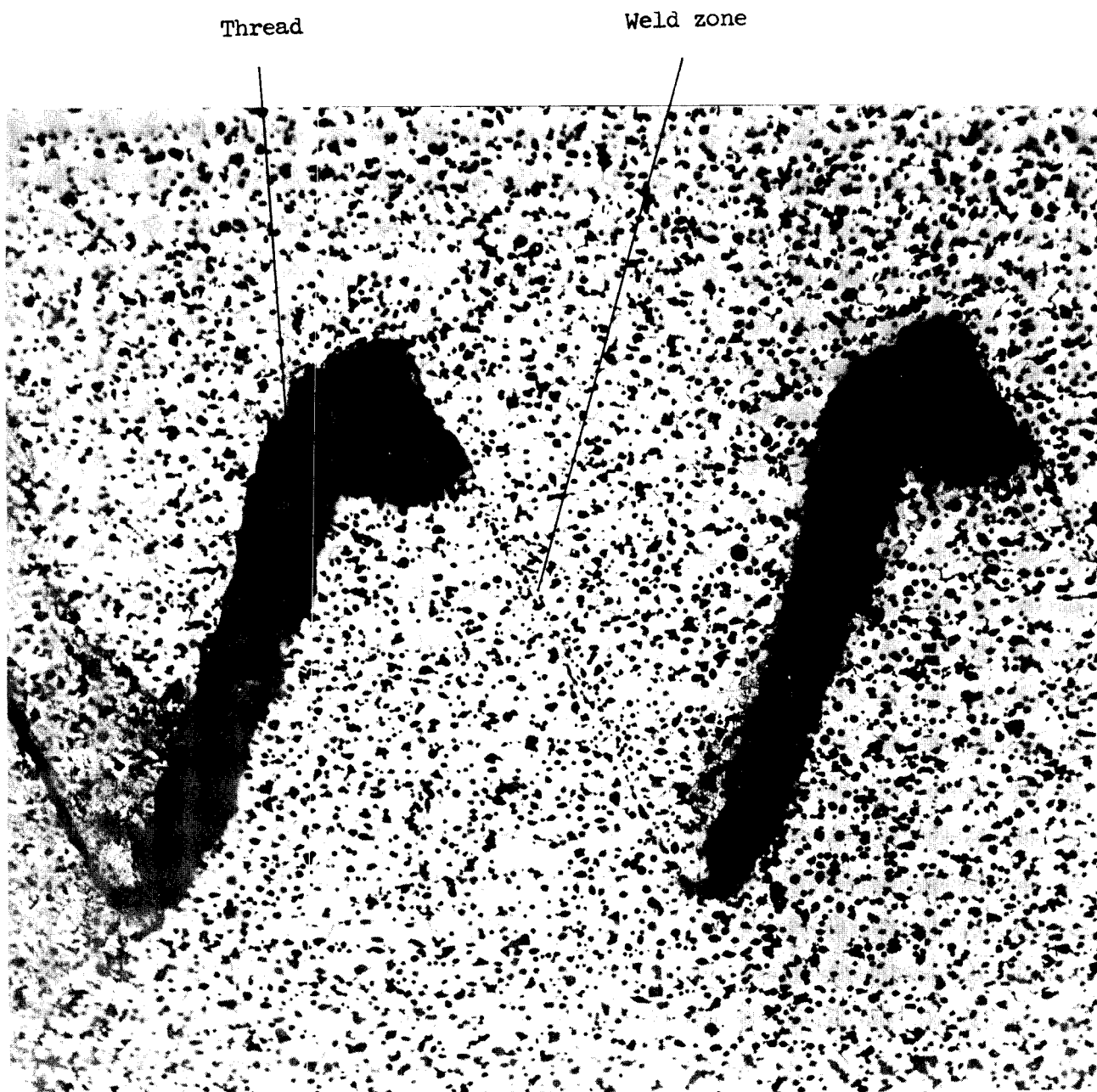


Figure 24.- Bolt and nut assembly before and after exposures at 2500° F for 1 hour. The shank broke in an attempt to disassemble bolt and nut after exposure.

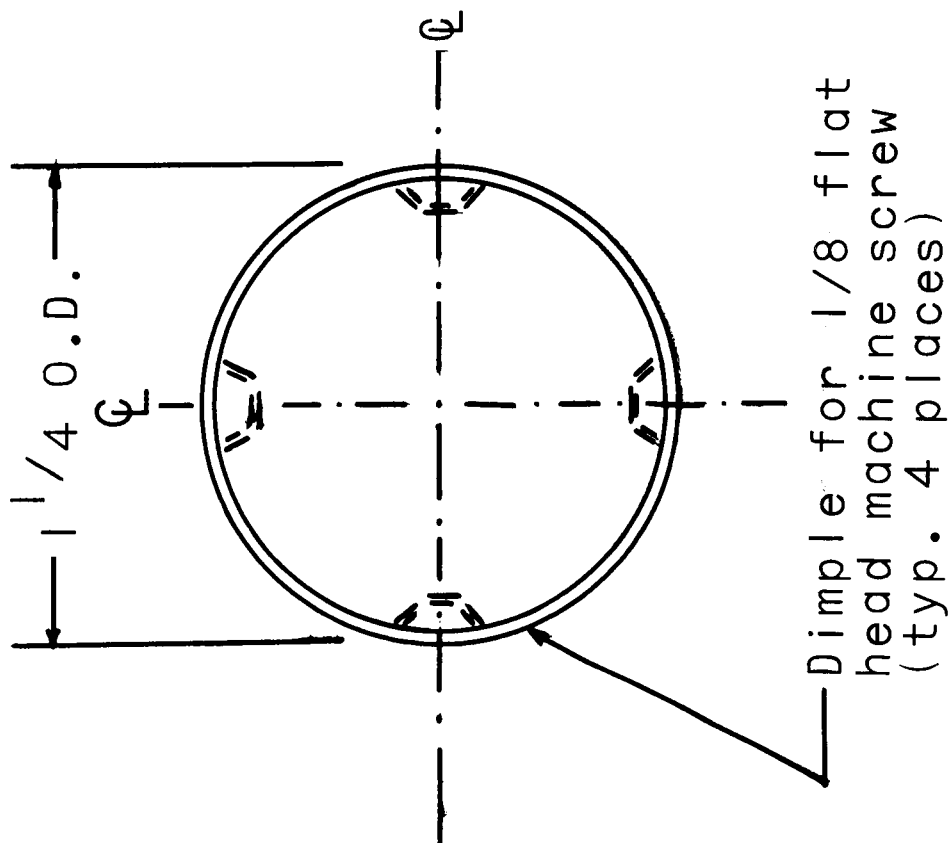
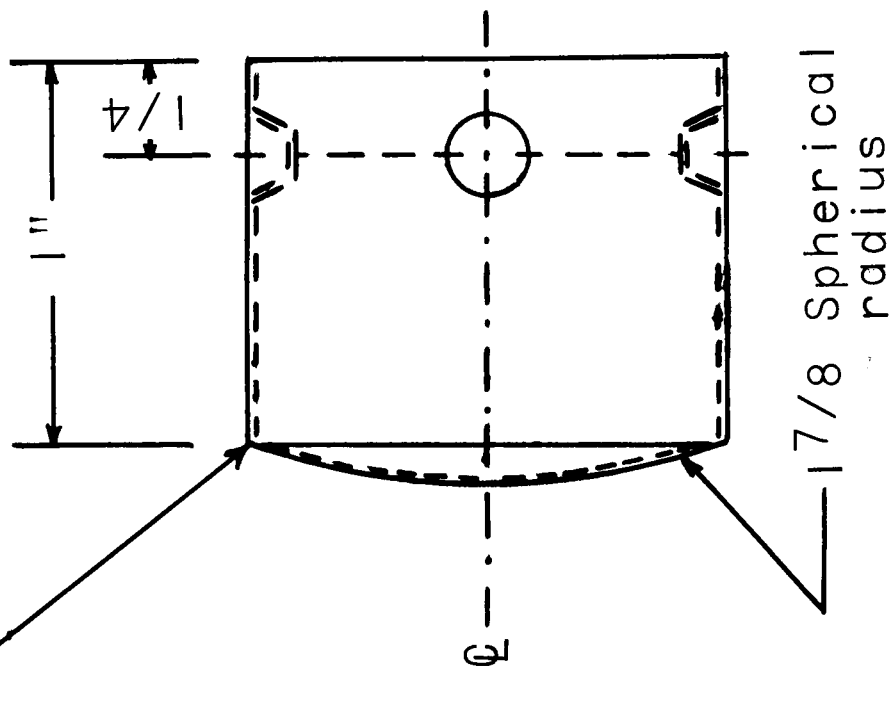
L-63-75



L-63-76

Figure 25.- Microstructure showing the threads of a sectioned bolt and nut assembly after exposure for 1 hour at 2500° F. x100.

Electron beam butt
weld all around



Dimple for 1/8 flat
head machine screw
(typ. 4 places)

Figure 26.- Proposed dynamic-oxidation specimen for testing in the hypersonic wind tunnel. Specimen failed on fabrication.